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# THE STRUCTURE OF ATOMS





# THE STRUCTURE OF ATOMS

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## PREFACE

THE contents of this volume (which has been revised and brought up to date for the English translation) formed the subject of a series of lectures delivered at the Farbwerken vorm. Fr. Bayer & Co. at Leverkusen in September, 1919.

When I was asked to give to the chemists at these works an account of the most recent advances in chemistry I was not for a moment in doubt as to the choice of a subject, namely, the astonishing advances in our knowledge of the fine structure of matter which have been made during the last few years. Chiefly by the work of the physicist a new region has here been revealed to us ; a fertile country which even now has yielded many blossoms and fruits and many more most promising buds, a veritable Wonder-garden, as yet little known to chemists but one which on closer acquaintance can offer a wealth of inspiration and enjoyment. It is, however, by no means easy for the chemist to wander in this garden and pursue knowledge along its winding paths, for the way is set about with the thorns of theoretical physics and mathematics. In this short guide an attempt has been made to put aside these thorns and bring into the foreground the point of view of experiment. The essential principles of this branch of knowledge and its historical development are here simply but fully described.

For those readers who wish to go more deeply into the subject a list of suitable books is given at the end of the volume.

The title "Ultrastrukturchemie" explains itself. Just as Ultramicroscopy takes us beyond the smallest particles seen in the ordinary microscope so in "Ultrastrukturchemie" we go beyond the boundaries of ordinary structural chemistry into the realm of the smallest building stones of matter, and discuss the laws governing the structure of atoms as well as molecules.

## TRANSLATOR'S NOTE

**I**N preparing the English translation I have, with the author's approval, made one or two slight changes from the original text. These consist of a division of the book into chapters and the introduction of a diagram and description of a Röntgen ray bulb.

The title "Ultrastrukturchemie" can scarcely be translated literally; it has therefore been rendered "The Structure of Atoms."

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“C'est l'ignorance qui sépare les hommes  
et la science que les rapproche.”  
—PASTEUR

# THE STRUCTURE OF ATOMS

## CHAPTER I

### THE CHEMICAL ELEMENTS

#### *Older Views of the Nature of Matter*

FROM the earliest times man has endeavoured to gain some insight into the nature of matter, of the substances in Nature which are perceived by our senses. At first he pursued this knowledge on the fickle wings of imagination; only for a few hundred years has he followed the certain but slow and stony path of experiment.

Of all the sciences chemistry is most intimately concerned in these inquiries both on the theoretical and practical side. It is continually using the words "substance" or "matter" to express its most fundamental conceptions and its chief business is to study the changes which matter undergoes. When I was a student in the 'nineties most chemists believed that the laws of matter had found their essential and final expression in the familiar atomic and molecular theories. This was a fundamental error. To-day we know that this science is as yet only at the beginning of its development, and has been awakened to new life by the brilliant results of physical investigations.

In ancient times and in the Middle Ages there was no chemical knowledge in the modern sense of the term. The method of experimental investigation, self-evident, clear, and independent of hypotheses, was then unknown. The followers of Aristotle had no conception of that attitude of mind which Baeyer expressed characteristically in the words, "My investi-



gation has been designed not so much to determine whether or not I was right as to discover how substances behaved." On philosophical grounds, striving after the greatest possible unity of ideas, the ancient thinkers created a theory of the nature of matter which explained phenomena by reference to one or other of certain primary substances such as Fire (the Persian, Heraclitus), Water (the Egyptian, Thales), or Air, from which, according to Anaximenes, all liquid and solid substances could be produced by condensation or expansion. Empedocles for instance believed in a larger number of primary substances, namely Fire, Water, Air, and Earth. Such ideas taught by the Aristotelean school of philosophers had almost undisputed sway for more than fifteen hundred years. They reappear in the "Principles" mercury, salt, and sulphur, which the alchemists believed to be the basis of all substances.

### *Atomic Theories of the Ancients*

The older philosophers in considering the nature of matter discussed the question as to whether matter entirely filled space or whether it was composed of small discrete particles with interstices between them. In our text-books of chemistry we find the atomic theories of Leucippus and his friends, and those of the school of Democritus described as forerunners of Dalton's theory. These theories describe the smallest particles of matter as "atoms" (*ἄτομος*, indivisible) minute, undecomposable, rigid bodies, suspended and moving about one another in empty space, and by their aid they accounted for the phenomena of winds and waves, of fusion, evaporation, expansion by heat, etc.

### *Development of the Conception of Elements*

It is only about three hundred years ago since the fundamental ideas on which chemists rely to-day were first put forward. Van Helmont at the beginning of the seventeenth century was the real author of the word "gas," and was led to the opinion that chemical substances "contained" other simpler substances which could be prepared from them, e.g. copper sulphate "contains" copper, a method of expression

which even in our own time has led to much misunderstanding. Boyle a little later gave the definition of a chemical "ground-stuff" or element as we understand the term to-day. He recognized as an element a chemical substance which could not be further split up by chemical means.

### *Stoichiometry and Dalton's Atomic Theory*

Then came the time of Lavoisier, the chemistry of weighing and measuring and the discovery of the fundamental natural laws of combination. These by their simplicity and rigorous accuracy ranked alongside the physical laws of gravitation, etc., and made chemistry for the first time an exact science. Yet Berthelot (1748-1822) was of opinion still that chemical compounds might contain their constituents in any variable proportion. About the same time J. R. Richter (1792) published his "Foundations of Stoichiometry or the Art of Measuring the Chemical Elements," with the Biblical guiding principle that "God has ordered all things by measure and number and weight." In 1802 Dalton put forward the new atomic theory based on the experimental laws of combination. The great practical and technical importance of an accurate knowledge of relative atomic weights has caused them to be determined with the greatest possible precision by the careful analysis of highly purified substances or by physical methods (Berzelius, Stas, Richards, Guye, etc.).

### *Molecular Theory*

The atomic theory was for many years incomplete for chemists did not, at first, perceive the significance of Avogadro's molecular hypothesis. We shall consider later the laws of chemical combination and valency and the development of structural chemistry which seeks to determine the arrangement of atoms in the molecule.

### *Prout's Hypothesis*

As soon as it was seen clearly that there were several uncomposable substances or elements chemists began to make hypotheses as to whether or not they were all derived from one kind of primary substance. Thus Boyle was of opinion

that all the elements were related to one another in this way. On the other hand Berzelius, two hundred and fifty years later, was firmly convinced that they had nothing in common. In 1815 Prout, recognizing that many atomic weights are whole numbers if the atomic weight of hydrogen be taken as unity, came to the conclusion that all atomic weights must be simple multiples of that of hydrogen and that this element is the primitive substance of which the other atoms are built up. As atomic weights were determined with greater accuracy Prout's hypothesis could no longer be accepted, for it was found that on the hydrogen scale some atomic weights were certainly not whole numbers and in some cases, e.g. chlorine (35.5) had values exactly the mean of two successive numbers. The hypothesis was retained for a while in a modified form in which a primary substance with smaller particles of atomic weight 0.5 or 0.25 was assumed, but even this modification could not eliminate differences between theory and experiment. Later theories which brought in carbon, hydrogen, helium, and the ether as primary substances were no more successful.

*Are the Atoms composed of Smaller Particles ?*

To-day, however, we cannot but recognize the fact that there is a certain element of truth in Prout's hypothesis. It is certainly remarkable that so many atomic weights should be approximately whole numbers, many more than would be predicted from a chance distribution over the possible range of values. This is obvious if, for example, one considers the smaller atomic weights. The most recent and accurate values for these (on the scale  $O = 16$ ) are :

H, 1.008 ; He, 4.0 ; Li, 6.94 ; Be, 9.1 ; B, 11.0 ; C, 12.005 ; N, 14.01 ; O, 16.00 ; F, 19.0 ; Ne, 20.2 ; Na, 23.00 ; Mg, 24.32 ; Al, 27.1 ; Si, 28.3 ; P, 31.04 ; S, 32.06 ; Cl, 35.46.

Of these seventeen numbers thirteen are whole numbers within a tenth of a unit. This can scarcely be due to "chance" and can only be accounted for by the view that all atoms contain a common primary particle of the same mass.

It has long been known that certain optical phenomena support this conception of the common origin of atoms and

are not in agreement with the older view that they are rigid, unalterable bodies. Thus many elements when heated in the bunsen flame emit characteristic radiations which must be ascribed to the vibration of parts of the atom.

### *Are the Elements Interconvertible ?*

If it is assumed that the different atoms are built up of similar particles then a question of great practical importance immediately arises, namely, "Can different atoms, i.e. elements, be converted into one another?" Our predecessors in the Middle Ages, the alchemists, believed that an affirmative answer to this question was a self-evident truth. For eight hundred years they endeavoured to bring about a transmutation by the use of certain reagents to which they gave imposing names, such as the Touchstone, the Great Elixir, the Red Tincture, the Magisterium Universale or Fermentum, the Quinta Essentia, etc. In spite of all their labours, from the authentic records which have come down to us it is in the highest degree improbable that they ever achieved a successful transmutation of elements. More recent claims to having brought about an interconversion of elements, e.g. phosphorus into arsenic, boron into silicon, etc., have been shown to be due to inaccurate experiments. Consequently Lockyer's Evolution theory has received but little support. This theory, based upon observations of the spectra of the hotter stars, assumes that at high temperatures only the simplest atoms, or parts of atoms (e.g. hydrogen, "protocalcium," "protomagnesium," oxygen, etc.) can exist, and that these condense together progressively on cooling to form the more complex atoms.

### *Anticipations of the Periodic System*

Any relationship between the masses (expressed as atomic weights) and the chemical and physical properties of the atoms of the elements would obviously be of great significance in connection with the question of a genetic connection between the elements. Such relationships have been known for more than a hundred years. Döbereiner in 1817 pointed out the existence of "Triads" or groups of three chemically similar

PERIODIC SYSTEM OF THE ELEMENTS AFTER MENDELEEFF (ENLARGED).

Series	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
	—	—	—	—	RH <sub>4</sub>	RH <sub>3</sub>	RH <sub>2</sub>	RH	Highest hydrogen compound
	R	R <sub>2</sub> O	RO	R <sub>2</sub> O <sub>3</sub>	RO <sub>2</sub>	R <sub>2</sub> O <sub>5</sub>	RO <sub>3</sub>	R <sub>2</sub> O <sub>7</sub>	RO <sub>4</sub> Highest oxide
1		1 H							
2	He 4	Li 7	Be 9	B 11	12 C	14 N	16 O	19 F	1st short period
3	Ne 20	Na 23	Mg 24	27 Al	28 Si	31 P	32 S	35.5 Cl	2nd short period
4	A 40	K 39	Ca 40	Sc 45	Ti 48	V 51	Cr 52	Mn 55	Fe 56 Co 59 Ni 59
5		64 Cu	65 Zn	70 Ga	72 Ge	75 As	79 Se	80 Br	1st long period
6	Kr 83	Rb 85	Sr 88	Y 89	Zr 91	Nb 94	Mo 96	—	Ru 102 Rh 103 Pd 107
7		108 Ag	112 Cd	115 In	119 Sn	120 Sb	128 Te	127 J	2nd long period
8	X 130	Cs 133	Ba 137	La 139	Ce etc. 140-178	Ta 182	W 184	—	Os 191 Ir 193 Pt 195
9		197 Au	201 Hg	204 Tl	207 Pb	208 Bi	—	—	3rd long period
10	Em 222	—	Ra 226	—	Th 232	—	U 238	—	

elements whose atomic weights were such that one of them was the mean of the other two, e.g. Calcium (40), Strontium (88.5), Barium (137).  $88.5 = (40 + 137)/2$ . These limited rules reached their full development in the natural or periodic system of the elements due to Lothar Meyer and Mendeléeff, which was partly anticipated by the work of many earlier investigators. Of these the most important are the tables of elements of Gmelin (1843) based on chemical similarity, those of de Chancourtois (1862), of Lothar Meyer himself (1864), and of Newlands (1863–1866, Law of Octaves). Mendeléeff's table is shown on p. 6 enlarged to include the more recently discovered elements. In this table the elements are arranged in the order of their atomic weights and after a certain number, at first eight, later a larger number, so as to give "short" and "long" periods, chemically similar elements occur in similar positions. The chemical properties of the elements and many of their physical properties are functions of the atomic weight.

Mendeléeff immediately drew many far-reaching conclusions from his newly-discovered law. Beryllium, which had previously been regarded as a trivalent element with an atomic weight of 13.5, could find no place in the periodic system. Without hesitation Mendeléeff asserted that this element must be divalent and have an atomic weight of 9 when a place could be found for it in the table. This change was soon verified by experiment. Indium and Uranium were treated similarly; these elements were formerly supposed to be divalent, but to fit them into the table it was necessary to regard them as tri- and tetra-valent respectively. A still greater triumph was the prediction of the properties of elements which were then unknown. Since gaps were found in the periodic system, Mendeléeff foresaw the existence of new elements to fill them. To these he gave names derived from those of the element which stood above them in the table, e.g. Eka-aluminium, Ekasilicon, Ekaboron, (Eka = 1, Sanscrit) and predicted many of their physical and chemical properties. These elements (Gallium, Germanium, Indium) were soon discovered, and were found to possess exactly the expected properties. In the following table Germanium, discovered by Winkler in 1886, is compared with Mendeléeff's predictions for Ekasilicon,

	Ekasilicon.	Germanium.
Atomic weight . . . . .	72	72.5
Density of metal . . . . .	5.5	5.47
Oxide . . . . .	EsO <sub>2</sub>	GeO <sub>2</sub>
Chloride . . . . .	EsCl <sub>4</sub>	GeCl <sub>4</sub>
Boiling point of chloride . . . . .	below 100°	86°

Mendeléeff's prophetic description of unknown elements has been with justice compared to the discovery of the planet Neptune by Leverrier, who from the perturbations of other planets inferred its existence and calculated its orbit so accurately that Galle found it exactly in its predicted position.

As time went on the periodic system received further support from experiment, as all the elements discovered later could be smoothly fitted into it. The inert gases found their place as a new group and the radio-active elements in vacant spaces between known elements.

### *Irregularities in the Periodic System*

Yet the periodic system was not everywhere consistent and in some places its fundamental principle had to be sacrificed to avoid obvious misplacements. Argon from its chemical properties must, without doubt, be placed with the inert gases, while potassium must certainly be regarded as a member of the family of the alkali elements. Yet the atomic weight of potassium, 39.10, is less than that of argon, 39.88, hence potassium should really be placed before argon in the table. The same thing happens with the pairs of elements tellurium, 127.5, and iodine, 126.92, cobalt, 58.97, and nickel, 58.68. In each case the atomic weights would give these elements places in the system in the reverse order to that demanded by their chemical properties. At first chemists were firmly convinced of the accuracy of the underlying principle of the system and thought that these irregularities were due to errors in the determination of atomic weights and would disappear when these numbers were more accurately known. This, however, was not the case. New and trustworthy determinations of the questionable atomic weights showed that, in these cases, there was, undoubtedly, an unexplained divergence from the general law. In other ways, also, the periodic

system was found to be defective. The three triplets of elements, iron-cobalt-nickel, ruthenium-rhodium-palladium, and osmium-iridium-platinum, form an exception to the rule in this group. Further, it has not been found possible to devise a satisfactory arrangement of the fourteen elements of the so-called rare earths which have atomic weights ranging from 139 (Lanthanum) to 175 (Lutetium). The high hopes which the discovery of the periodic system had aroused were thus not fulfilled. A natural law of the greatest importance had been dimly perceived but was not yet fully known. The properties of the elements were, on the whole, a periodic function of their atomic weights, but there were exceptions.

In spite of these defects the periodic system is still the best and simplest foundation for a classification of the elements. The chemical characteristics of an element are fixed with certainty by its position in the system. The group of the chemically inert gases forms a dividing line on each side of which are found the most chemically active elements. On one side are the strongly electro-negative halogens, etc., and on the other the strongly positive alkali metals. The elements which stand midway between two consecutive rare gases, e.g. carbon, do not display any sharply-defined polarity or chemical character. As the atomic weight increases the electropositiveness of the elements diminishes if one passes along a horizontal "period" but increases as one descends a vertical "group."

Several attempts have been made to modify the periodic system of Lothar Meyer and Mendeléeff so as to avoid its defects and include all the elements in one clear generalization. New arrangements in spiral, zig-zag, and other forms have been suggested, but none of them are entirely satisfactory.

### *Implications of the Periodic System*

The periodic system shows definitely that there is a genetic connection between the elements and that therefore particles of matter smaller than atoms must exist from which the atoms are built up. It is difficult to explain in any other manner why a certain increase in the mass of an atom produces a repetition of similar chemical properties, and why, from a group of chemically similar elements, a step by step increase of mass



gives other groups of chemically similar elements. These facts suggest at once that after a certain increase in number the sub-atomic particles arrange themselves in a similar manner and that similar atomic structure corresponds to similar chemical properties. In discussing these questions in chemical lectures years ago one was glad to recall the beautiful experiments of Mayer on the regular arrangement of particles free to move under the influence of certain attractive and repulsive forces. Here again a remarkable recurrence of similar arrangements is found. Mayer used small magnets, e.g. magnetized

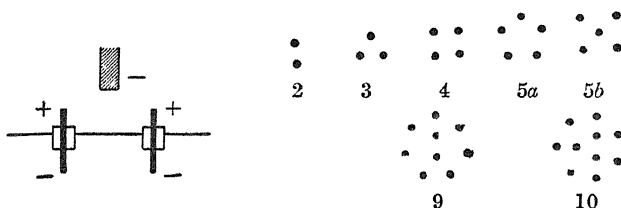


Fig. 1.

needles, mounted in corks and floated on the surface of water with all the positive poles uppermost (see Fig. 1, left). The magnets moved away from one another owing to the repulsion of similar poles. If the negative pole of a strong magnet is brought near the positive poles of the needles it will tend to draw them together. The floating magnets therefore take up a definite grouping in which this attracting force is in equilibrium with their mutual repulsion. For a definite number of magnets there is usually one stable grouping; in some cases more than one arrangement is possible. Fig. 1 shows on the right the positions taken by 2, 3, 4, 5, 9 and 10 floating magnets. It is found that 3 magnets arrange themselves in the form of an equilateral triangle, 4 as a square, 5 a regular pentagon, or a square with the fifth magnet at the centre, 9 a regular heptagon with two magnets inside, 10 a regular heptagon with three magnets inside arranged as an equilateral triangle, and so on. What is of particular interest here is the periodic recurrence of similar arrangements, e.g. the pair of magnets in groups 2 and 9, and the equilateral triangle in groups 3 and 10, etc. Let us suppose that sub-atomic particles are substituted for the magnets and that they also

arrange themselves in a definite equilibrium grouping under the influence of forces of attraction and repulsion. In this way we obtain a working model of the kind of atom structure which may possibly be the real underlying factor determining the periodicity of the elements.

### *The Size of Atoms and Molecules*

With the progress of science the atomic and molecular theories became less and less hypothetical in character. Many of the more recent investigations, mostly in physics, have forced upon scientists the conclusion that the atoms and molecules which the chemist uses to account for certain chemical relationships of mass and volume have a real existence as separate entities. Their absolute size has been measured by several different methods with very concordant results. Chemists knew already that a single molecule must be very small. Thus Berthelot found that a hundred thousand billionth part of a grain of musk could be detected by its odour, hence a molecule of musk cannot have a greater weight than this. Zsigmondy examined a solution of colloidal gold in which the particles were too small to be seen even with the ultra-microscope, and counted the number in a given volume by "developing" them with a solution of gold salt until they "grew" large enough to be detected. From the number thus found and the known gold content of the original solution he calculated the mean weight and diameter of the particles of colloidal gold and for the diameter obtained the figure  $0.8 \mu\mu$ . (i.e.  $0.8 \times 10^{-7}$  cm. or 0.8 millionths of a millimetre). Colloidal solutions of this kind have properties approaching those of true solutions in which dissolved substances are split up into separate molecules. It follows, therefore, that these colloid particles cannot have a much greater diameter than that of a single molecule or atom of gold. As a matter of fact the radius of a molecule has been found to be about  $0.1 \mu\mu$ .

The general physical and mathematical principles which lead to methods of estimating accurately the size of atoms and molecules cannot be discussed here in detail. It will be sufficient to mention the physical phenomena with which they deal. These include the kinetic theory of gases, the so-called Brownian movement of colloidal particles suspended in liquids

or gases (discovered with pollen grains by the botanist Brown in 1827), and the determination of the elementary unit charge of electricity. These elementary units or electrons will be referred to again later. It is a most remarkable fact that some half-dozen different and entirely independent methods of determining the size of molecules all lead to the same result. Obviously our assumptions about atoms are in agreement with a very wide range of experimental data. Some idea of the magnitude of molecules is given by the two numbers which follow. The mass of a hydrogen molecule is  $3.24 \cdot 10^{-24}$  gm. It bears the same ratio to the mass of a gram of hydrogen (about 12 litres at ordinary temperature and pressure) as one kilogram does to the mass of the earth. In a cubic centimetre of hydrogen gas at  $0^{\circ}$  C. and 760 mm. pressure, there are  $25 \times 10^{18}$  (i.e. 25 trillion) molecules. From Avogadro's hypothesis this is the number of molecules in 1 c.c. of any gas. These constants are called Loschmidt's numbers in honour of the investigator who first showed how to determine the magnitude of molecules.

We have now learned something of the standpoint of the atomistic view of matter up to the time at which its more recent and prolific development began. The newer work can be more readily described if we classify it according to the experimental methods which have been used. These fall chiefly into three groups, those of optics, of electricity, and of radio-chemistry.

## CHAPTER II

### OPTICS

THE older science of optics was at first concerned with the study of ordinary visible light of wave length  $0.4-0.8\mu$  ( $10^{-4}$  cm.). Later the neighbouring regions of "light" invisible to our eyes were gradually explored; the infra-red rays of longer wave-length and the short ultra-violet rays. [The debt which chemistry owes to optics will be realized if one thinks of the work which has been done on the colour of chemical substances, on refraction, dispersion, rotation of polarized light, spectrum analysis, etc. By the methods developed by spectroscopy the optical characteristic of a ray of light, i.e. its wave-length, can be measured with extreme accuracy. Light can be broken up into its constituent rays by a prism spectroscope or by means of a "grating." The first type of instrument is usually employed by chemists as it is sufficiently accurate, is cheaper, and is not so easily affected by the air of the laboratory as the more delicate grating spectroscope. This latter instrument is used by the physicist for more accurate investigations. Its action depends upon the decomposition of light by means of a grating which consists of a large number (up to 2,000 per mm.) of fine parallel lines ruled on speculum metal. Light reflected from the grating suffers a certain bending or "diffraction" which always is evident when a ray of light passes by an obstacle of the same order of magnitude as the wave-length. A part of this deflected light is destroyed by interference with the undeviated rays; in certain directions, however, where the "phase difference" between the two rays is equal to the wave-length the intensity is increased.]

[White light is composed of many different wave-lengths.

In the spectroscope it produces all the colours of the rainbow, or what is termed a continuous spectrum. Coloured light contains only certain ranges of wave-length and its spectrum is composed of a number of coloured lines or bands which, in the spectroscope give separate images in definite positions. Monochromatic light consists of rays of uniform wave-length.

The radiations emitted by a glowing gas, e.g. the vapour of a salt heated in a bunsen flame or hydrogen in a Geissler tube, have characteristic wave-lengths for each radiating element. Bunsen and Kirchoff's great discovery of spectrum analysis was based on this fact. If white light is passed through a glowing vapour then those radiations are absorbed which the vapour itself emits, and dark lines are produced in what was previously a continuous spectrum. This is the well-known explanation of the dark lines in the spectrum of sunlight.

Quite early in the history of the science the radiation emitted by incandescent substances was referred to vibrations originating in the substance and transmitted through space as light. These vibrations must start from the atoms of the element in question for it was found that the character of the radiation did not depend at all upon the structure of the molecule.<sup>1</sup> Thus all sodium compounds when heated in the bunsen flame give the same monochromatic yellow light. These facts give further support to the view that atoms contain smaller particles which are free to move. Still stronger evidence for this hypothesis was obtained when Zeemann discovered in 1897 that the spectrum altered a little when a radiating substance was subjected to magnetic forces (Zeeman effect). The vibrating particles which excite the radiations are therefore affected by magnetic forces and also, as was found later, by electrical fields (Stark effect).

Some elements, e.g. hydrogen, helium, and sodium, give comparatively simple spectra, others, e.g. iron, give spectra exhibiting thousands of lines. All these spectra have been thoroughly studied by physicists and the wave-length or the number of vibrations per second (frequency) for each individual line measured with great accuracy. Frequency and wave-length are simply related to one another, for all the radiations,

<sup>1</sup> It should be mentioned that in addition to the "atomic" radiations referred to above radiations due to molecules are known.

whatever their frequency, travel with the same velocity, namely 300,000 kilometres per second.

### *Regularities in Spectra ; Balmer's Formula*

Regular relationships between the different lines of a spectrum were zealously sought for, but for many years the real regularities were overlooked because wrong methods and hypotheses were used. For instance, Lecoq de Boisbaudron, the well-known discoverer of Gallium, assumed that similar relations would hold in optics as in acoustics where the frequencies of the principal tone and the overtones are related, as 1 : 2 : 3 : 4, etc. Things were not so simple in this case. Balmer in 1885 first discovered a regularity of an unexpected type. He showed that the wave-length of a group of lines in the spectrum of hydrogen could be calculated by the formula  $\lambda = \frac{K m^2}{m^2 - 4}$

where K is a constant (3646.13) and  $m$  the whole numbers from 3 to 31 in succession. The table below shows the very striking agreement between the numbers calculated by this formula and the observed wave-lengths.

$$\lambda = 3641.13 \frac{m^2}{m^2 - 4}$$

Line.	$m$	calc.	obs.
H $\alpha$ . . .	3	6564.96	6564.97
H $\beta$ . . .	4	4862.93	4862.93
H $\gamma$ . . .	5	4341.90	4342.00
H $\delta$ . . .	6	4103.10	4103.11
H $\epsilon$ . . .	7	3971.4	3971.4
H $\zeta$ . . .	8	3890.3	3890.3

The cause of these very remarkable regularities puzzled physicists for many years. It was found that other lines in the spectrum of hydrogen and certain groups of lines in the spectra of other elements could be predicted by expressions of a similar mathematical form. Groups of lines related to one another in this manner are termed "line series" or more shortly "series."

### *Röntgen Ray Optics*

In 1912 a great extension of optics took place, of such importance that this date may well be regarded as the begin-

ning of a new epoch in physical and chemical investigation. This advance was the development of a kind of ultra-optics, the optics of Röntgen or X rays, in which the Röntgen rays take the part played by light in the older science.

These rays, discovered by Röntgen in 1895, are produced when electricity is passed through a highly attenuated gas. Fig. 2 shows one type of bulb used for the production of Röntgen rays. When a high-tension discharge from the secondary of an induction coil is passed through the bulb, electrons (see p. 28) are shot off from the cathode C and travelling with a high velocity strike a point on the anticathode A which is

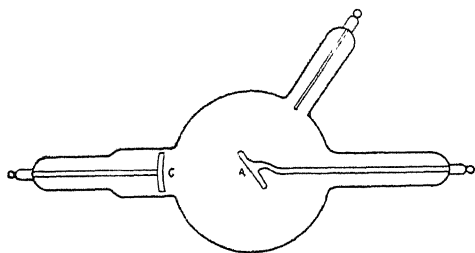


Fig. 2.

usually made of a metal with a high melting point, e.g. tungsten. The Röntgen rays originate at the point at which the electrons strike the anticathode and spread out from it in all directions with the

velocity of light.

After the original work of Röntgen, the investigation of these rays progressed comparatively slowly. For some time it was not certain that the rays were really radiation in the sense of which Huygen understood the term, i.e. it was doubtful whether they were vibrations analogous to those composing light on Huygen's theory or whether they consisted of streams of material particles, a view which Newton had used to account for ordinary light. On the whole, the balance of evidence was in favour of the first hypothesis. In the earlier dispute which had raged between the emission and undulatory theories of light a very strong argument for Huygen's wave theory was the phenomenon of the diffraction of light round an obstacle. This diffraction takes place, for example, with the gratings mentioned above and can readily be detected when the "grating distance," i.e. the distance between adjacent lines, is about twenty to fifty wave-lengths. The phenomenon of diffraction can only be explained satisfactorily on the wave theory.

*von Laue's Discovery*

The first successful experiment of this kind with Röntgen rays was devised by von Laue, who used the finest possible kind of grating which Nature has provided in the structure of crystals. Von Laue assumed that Röntgen rays were the same kind of vibrations as common light, but of much smaller wave-length. On this view one would no more expect them to be diffracted by an ordinary spectroscope grating than one would expect to produce a spectrum from ordinary light by means of the rails of a fence. It was necessary, therefore, to find a grating with very much smaller intervals than those usually employed. Such gratings were found in crystals which, according to the work of mineralogists and physicists, had their molecules or atoms arranged regularly in a definite lattice or space grating. From the known size of molecules the grating distance of these lattices could be estimated, and was found to be about  $10^{-7}$  to  $10^{-8}$  cm. This was just about the size which von Laue thought necessary to produce a measurable diffraction of Röntgen rays. When put to the test of experiment all his anticipations were realized; with these fine gratings Röntgen rays were diffracted in the same way as light is diffracted by the coarser grating of the spectroscope. It was therefore demonstrated that Röntgen rays were trains of vibrations and, by using suitable apparatus, could be made to behave in much the same manner as common light. The study of Röntgen ray optics has led to many great advances in knowledge during the last few years. We shall only discuss those which are relevant to our subject.

The average wave-length of the Röntgen rays is about one-thousandth that of ordinary light, or about  $10^{-8}$  cm. ( $\frac{1}{10,000,000}$  mm., the Ångstrom unit of optics). The frequency of Röntgen rays is therefore a thousand times greater than that of light. Röntgen rays covering a range of different wave-lengths are known. The Röntgen tube produces both "hard," penetrating rays of shorter wave-length and "soft" rays of longer wave-length. The terminology of optics has been pressed into service for the description of these rays and one speaks of "white" Röntgen radiation, containing all wave-



lengths, and of "coloured" and "monochromatic" rays. The ordinary Röntgen bulb produces in addition to a weak "white" radiation, an intense "coloured" radiation whose frequency depends upon the nature of the anticathode. The later advances of Röntgen ray optics have been made possible by great improvements in the apparatus used to produce the rays. Two modern types of Röntgen bulb are those devised by Lillienfeld and Coolidge, which are very highly exhausted and used for the production of the cathode rays emitted from electrically heated cathodes.

### *Röntgen Ray Spectroscopy*

Methods of investigating the spectra of Röntgen rays were soon worked out, and in a few years the wave-lengths of individual lines could be measured with a high degree of accuracy.

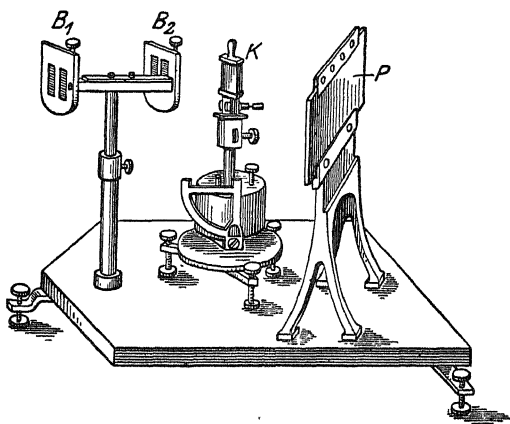


Fig. 3.

For these measurements an apparatus similar to that used in ordinary spectroscopy is employed (Fig. 3). By means of slits  $B_1$  and  $B_2$  with leaden jaws, a narrow beam of the rays is isolated and

allowed to fall on a crystal plate  $K$  which acts as a grating. Here it is diffracted and forms a spectrum which, of course, cannot be observed by the eye, but has to be recorded on a photographic plate  $P$ . Röntgen ray spectra are in general very similar to ordinary spectra and show a number of lines of sharply defined wave-length. These lines are always few in number: the complicated spectra found for some elements in the ordinary way are not observed with Röntgen ray spectra. Fig. 4 shows the Röntgen spectrum of the characteristic radiation of platinum (the  $L$  radiation). To excite Röntgen rays in this metal by absorption it is neces-

sary to use radiation of a definite wave-length which can be produced by a tube with a copper anticathode. The primary "copper" radiation is said to produce a secondary "fluorescent" Röntgen radiation in the platinum. The rays whose spectrum is shown in Fig. 4 were produced in this way.

Absorption spectra of Röntgen rays have also been investigated and are produced when the "white," radiation of a Röntgen bulb is passed through a metal, etc., before entering the spectroscop. The wave-lengths of the lines in the absorption spectra correspond exactly to those in the "fluorescent"

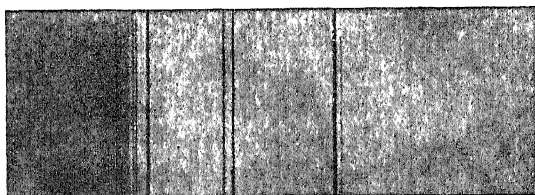


Fig. 4.

spectrum, so that this much easier experimental method can be used to measure the characteristic radiations.

Röntgen ray spectroscopy has already added greatly to our knowledge of the nature of elements. Most<sup>1</sup> elements can be made to emit "fluorescent" rays by exciting them with a primary radiation which must be of smaller wave-length than the secondary Röntgen rays it produces. Under these circumstances each element gives its own characteristic radiation and spectrum whether it is in the form of the free element or combined or alloyed with other elements. Thus brass gives the spectra of copper and zinc and sodium chloride those of sodium and chlorine.

#### *Regularities in Röntgen Ray Spectra*

The investigation of the Röntgen ray spectra of a number of elements has led to the discovery of a simple relationship between the position of an element in the periodic system and the nature of its characteristic Röntgen spectrum. The position of an element in the periodic table is called its "atomic

<sup>1</sup> The elements of smaller atomic weight up to 23 (Na) give no Röntgen ray spectra.

number." Hydrogen has the atomic number 1, helium 2, lithium 3, beryllium 4, boron 5, carbon 6, and so on. It was first discovered by Moseley that certain groups of lines (here called "series") were found in all the spectra of a number of elements which occupy successive positions in the periodic system. These series of lines in the different spectra resembled each other very closely in many ways, e.g. the relative positions and intensities of the individual lines. The chief difference was in the wave-lengths; the whole series shifted towards the region of shorter wave-length

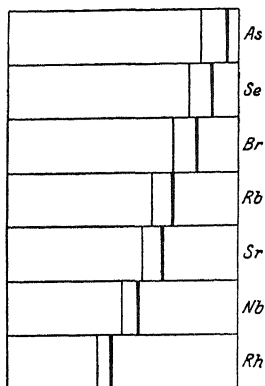


Fig. 5.

as one passed from one element to the next number of the periodic system.

Still further along the table elements with a certain larger atomic number gave a new characteristic series of lines of longer wave-length which again were displaced towards the shorter wave-lengths as the atomic number of the element increased. Physicists use letters to distinguish these series and speak of the K series, the L series, etc. Individual lines

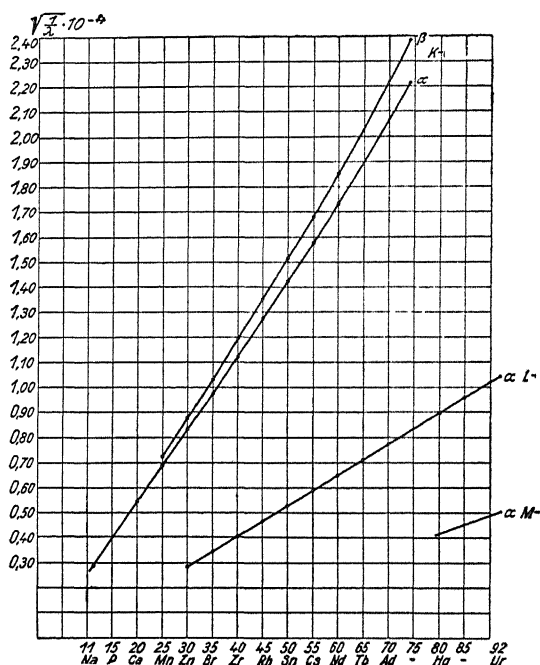


Fig. 6.

are indicated by suffixes, e.g.  $K\alpha_1$ ,  $K\alpha_2$ , etc. The most

important series discovered up to the present time are:—  
the K series consisting of five lines which has been observed from sodium to neodymium.

the L series of ten to fourteen lines from zinc to the last element in the periodic table, uranium.

the M series of seven lines from gold to uranium.

Fig. 5 shows the relative positions of the K spectra of a number of elements which occupy adjacent positions in the periodic system. Fig. 6 shows a remarkable relationship between the positions of the different lines and their displacement from one element to another. The atomic numbers of the elements are taken as abscissae; the ordinates are a function of the wave-length ( $\sqrt{1/\lambda} \times 10^{-4}$ ) the significance of which we must now discuss.

The vibration number, or frequency,  $\nu$ , is used generally, instead of the wave-length, to characterize the radiation which corresponds to an individual line. Since Röntgen rays, like visible light, travel with a velocity of 300,000 kilometres ( $3 \times 10^{10}$  cm.) per second, these two quantities are connected together by the equation

$$\nu = \frac{3 \times 10^{10}}{\lambda}$$

if  $\lambda$  is expressed in cms.

### *Moseley's Law*

A very simple numerical relationship between the frequency of corresponding lines in the Röntgen ray spectra of different elements and their atomic number,  $N$ , i.e. their position in the periodic system, was discovered by Moseley. This may be expressed by the equation  $\sqrt{\nu} = c(N - a)$  where  $c$  and  $a$  are constants. That is to say, the square root of the characteristic frequency is a linear function of the atomic number. This law is valid, not only for the K series, but for the L and M series as well. To perpetuate the name of its discoverer who, in 1914, at an early age, fell, a victim of the world war, it has been named "Moseley's Law of High Frequency Spectra" ("High frequency" because the Röntgen rays have a much higher frequency than common light).

Fig. 7 and Fig. 6 show graphically the relation between

$\sqrt{\nu}$  and  $N$ . The points representing the observed frequencies all lie on a straight line. This is only the case when  $\sqrt{\nu}$  is plotted against the atomic numbers. If, instead of these,

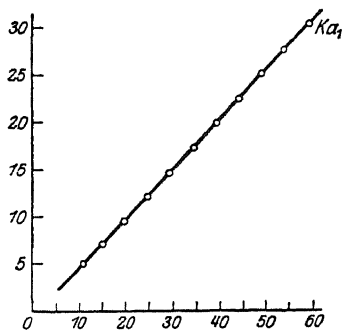


Fig. 7.

the atomic weights of the elements are used then, as Fig. 8 shows, a curve is obtained which approximates to a straight line, but deviates appreciably from it. It is a fact of the highest significance that atomic numbers and not atomic weights are involved in such an important natural law as that of Moseley. There must, therefore, be some constant for atoms which increases by equal amounts from

element to element in the periodic system and which determines the frequency  $\nu$ . The atomic weight of an element, on which the system was originally based, is not, as we have seen, a suitable constant. What

then is this mysterious something which runs parallel to the atomic numbers? We shall have to discuss this question again later and shall find that physicists regard the atomic numbers as being the number of units of free positive electricity in the nucleus of the atom. At present we will go no further

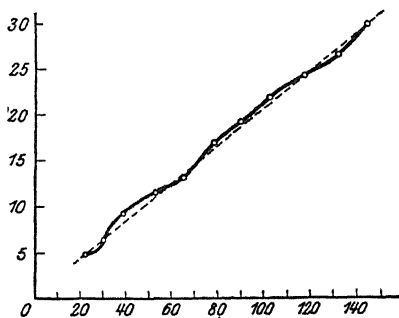


Fig. 8.

into the subject, but will cast a glance at our old periodic system in the light of this new knowledge. All the difficulties and inconsistencies have disappeared! If the system of the elements is based, not upon atomic weights, but upon atomic numbers, which can be determined experimentally by the application of Moseley's law to measurements of high frequency spectra then, as is shown by the table on page 23, the elements are arranged accurately in the order of their chemical properties. Argon comes before potassium, cobalt before

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Period	Series	0	Group VIII		Group I		Group II		Group III		Group IV		Group V		Group VI		Group VII	
			a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
I	1	2 He 4.00	3 Li 6.94	4 Be 9.1	5 B 11.0	6 C 12.00	7 N 14.01	8 O 16.00	9 F 19.0									
II	2	10 Ne 20.2	11 Na 23.00	12 Mg 24.32	13 Al 27.1	14 Si 28.3	15 P 31.04	16 S 32.06	17 Cl 35.46									
III	3	18 A 39.88	19 K 39.10	20 Ca 40.07	21 Sc 45.2	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93									
	4	26 Fe 27 Co 28 Ni 55.84 58.97 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 69.9	32 Ge 72.5	33 As 74.96	34 Se 79.2	35 Br 79.92									
	5	36 Kr 82.92	37 Rb 85.45	38 Sr 87.63	39 Y 88.7	40 Zr 90.6	41 Nb 93.5	42 Mo 96.0	43 —									
IV	6	44 Ru 45 Rh 46 Pd 101.7 102.9 106.7	47 Ag 107.88	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92									
	7	54 X 130.2	55 Cs 132.81	56 Ba 137.37	57 La 139.0	58 Ce 140.25	59 Pr 140.9	60 Nd 144.3	61 —	62 Sm 150.4	63 Eu 152.0							
	8	64 Gd 65 Tb 66 Dy 67 Ho 68 Er 157.3 159.2 162.5 163.5 167.7	69 Tm I 168.5	70 Yb 71 Lu 173.5 175.0	72 Tm II —	73 Ta 181.5	74 W 184.0	75 —										
	9	76 Os 77 Ir 78 Pt 190.9 193.1 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.2	83 Bi 209.0	84 Po (210.0)	85 —									
VI	10	86 Em (222)	87 —	88 Ra 226.0	89 Ac (226)	90 Th 232.15	91 Pa (230)	92 U 238.2										

nickel, and tellurium before iodine. Iron, cobalt, nickel, etc. and the rare earths all find a definite and fitting place in the system. Only five gaps remain to be filled by the discovery of new elements. These occur at atomic numbers 43, 61, 75, 85, and 87, and correspond to two elements of the manganese group, one metal of the rare earth group, a halogen, and an alkali metal. Chemists will probably discover all these elements in the future. The atomic number of the last of the known elements, uranium, is 92; this is the total number of chemical elements which can exist from hydrogen to uranium.

### *Determination of Crystal Structure*

In addition to these astonishing discoveries, of which chemists did not even dream a few years ago, Röntgen ray spectroscopy has rendered many other services to science. We have seen that it is possible to determine the nature of Röntgen rays by using a crystal as a grating. Conversely, by studying in detail the manner in which a crystal affects Röntgen rays, it is possible to ascertain the arrangement in space of the molecules and atoms and even the electrons which it contains.

### *Investigations of von Laue, Friedrich, and Knipping*

For the earliest work on this subject we are indebted to von Laue, Friedrich, and Knipping who, in 1912, demonstrated for the first time the interference of Röntgen rays by a crystal lattice. They caused a narrow pencil of Röntgen rays to pass through a thin slice of a crystal and fall on a photographic plate, both crystal and plate being fixed at right angles to the axis of the beam. The plate, when developed, showed a regular pattern of spots, the type of pattern being different for different crystals. Fig. 9 shows the pattern obtained with a crystal of zinc sulphide. The dark spot in the centre is produced by the primary ray which has passed through the crystal without deviation and around it is a regular pattern of spots produced by interference. These may be very numerous (up to 2,000 in one photograph) if Röntgen rays of very short wave-length are used. From the symmetry of the pattern one can draw conclusions as to the structure of the crystal and by rather tedious and complex calculations refer it to one or other of the thirty-two known classes of crystals.

This method can be used to determine structure even when one cannot obtain well developed crystals.

A most important advance was made in 1913 by the physicist Bragg and his son. They discovered that monochromatic Röntgen rays were reflected by a perfect crystal set accurately in the proper position. At a definite angle of incidence the equi-distant layers of particles in the crystal produced by reflection, or rather by interference, a brightening or an extinction of the reflected ray. This was not detected by photography but by using another well-known property of Röntgen rays. When these rays pass through a gas, e.g. air, they ionize it and make it capable of conducting electricity. The intensity of the reflected ray was measured by passing it into an ionization chamber which consisted of an outer casing maintained at a constant potential and an insulated inner disc; the quantity measured was the charge acquired by this disc when the reflected

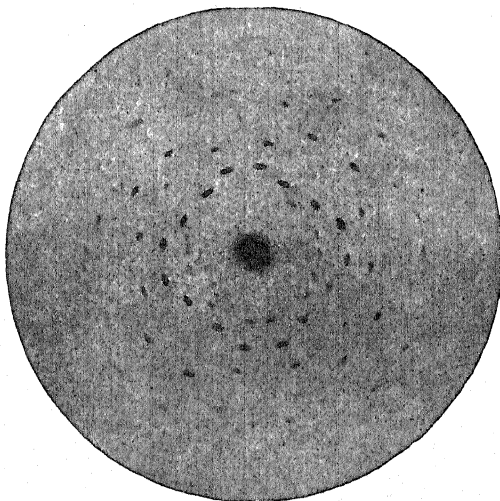


Fig. 9.

Röntgen rays were passed through the chamber. A large number of observations have to be made, with the crystal in a number of known positions. From these investigations, the first measurements of the wave-length of characteristic lines in high frequency spectra were obtained, and in addition the arrangement in space of the atoms in crystals of common salt, diamond, and many other crystals was worked out by determining accurately the distances between the planes of atoms in the crystal from which the particular space lattice can be deduced. This method is not, however, suitable for complicated crystals.



*Debye and Scherrer's Method*

With both of the methods described above it is necessary to assume a knowledge of the crystal system to which the substance under investigation belongs. A method has been devised by Debye and Scherrer which can be applied more generally and requires very simple experimental arrangements although its theoretical interpretation is more difficult. This method is shown diagrammatically in Fig. 10. The crystal powder—of which only a few cubic mm. are needed—is com-

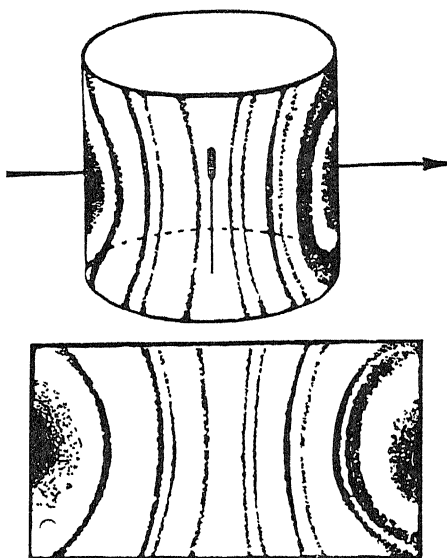


Fig. 10.

pressed into a little rod in which the crystals lie irregularly. This rod is placed at the centre of a hollow cylindrical chamber of about 5 cm. radius, the inner surface of which holds a film sensitive to light. A narrow pencil of Röntgen rays is admitted through an aperture covered with thin aluminium foil and passes through the substance as shown by the arrow in the diagram. A number of secondary rays are formed at angles which depend upon the

distances between the planes of the crystal lattice. These secondary rays have the form of conical surfaces and meet the cylindrical film in definite lines, which are recorded photographically. The lower part of Fig. 10 represents half of the film unrolled and shows the lines due to the secondary rays as well as the dark spot formed by the primary beam. Fig. 11 is a reproduction of an actual photograph obtained with graphite. The lines in these photographs become broader and fainter as the size of the crystals used approaches molecular dimensions. Even liquids, e.g. benzene,

which contain several atoms in their molecules give characteristic dark bands. The deduction of structure from the lines in the photographs involves the use of a special numerical technique which has been worked out by Debye and Scherrer. It is possible from one photograph to deduce the arrangement

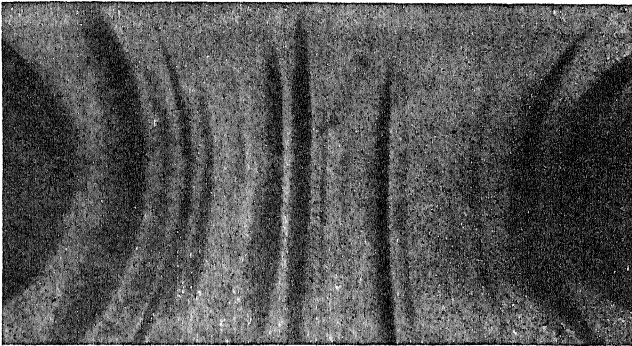


Fig. 11.

and distances of the atoms in a crystal even when nothing was previously known of the structure of the substance. Nay, further, Debye has gone beyond this and from measurements of the intensity of the lines, has inferred the number and arrangement of the still smaller electrons.

## CHAPTER III

### ELECTRICITY

**A**NOTHER branch of physics which has contributed largely to the elucidation of the structure of atoms is the more recent work on the nature of electricity. As early as 1881 Helmholtz, far in advance of his contemporaries, delivered his famous Faraday lecture on the atomic conception of electricity. From the close resemblance between Faraday's laws of electrolysis and the chemical laws of constant and multiple proportion, he argued that electricity had evidently atomic properties and must be made up of discrete particles or electrons. This very daring hypothesis has been fully justified by later work. To-day physicists account for electrical phenomena in material substances by means of these electrons and ascribe "action at a distance," e.g. electrostatic or electromagnetic induction, to disturbances in the ether travelling with the velocity of light, which are produced by the electrons.

#### *The Electron*

Only one kind of atom of electricity is definitely known, namely the electron of negative electricity. Positive electricity is only met with associated with ordinary chemical atoms in the form of ions, e.g.,  $H^+$ ,  $Na^+$ ,  $Cu^{++}$ .<sup>1</sup>

When electricity is passed through a gas at a very low pressure (about 0.01 mm.) cathode rays are produced which consist of nothing else but electrons. These rays were discovered by Plücker in 1859 and their characteristic properties described ten years later by Hittorf. Some years later came the better-known investigations of Crookes, who regarded the

<sup>1</sup> The hydrogen ion is often regarded as the positive electron.

rays as streams of material particles or corpuscles and not, as had been supposed previously, disturbances in the ether.

[When a cathode ray bulb is in action the electrons which form the cathode rays are shot off vertically from the surface of the cathode with a high velocity. They can be deflected from their rectilinear path by a magnet; hence they must carry an electric charge. By impact with material substances they can produce heat, light, and mechanical effects. If the rays fall on an insulated conductor they give it an electric charge. They also possess the property of ionizing gases through which they pass and making them conductors of electricity.]

The properties of cathode rays were at first very difficult to explain, but their nature was finally elucidated by the elaboration of new methods of investigation which were later applied to other charged particles, e.g. canal rays, gaseous ions, and the  $\alpha$  and  $\beta$  rays produced by radioactive substances. The methods of detecting electrons or these other charged particles fall into three groups. Electrical methods can be used, the rays being allowed to charge or discharge an insulated conductor. A chemical method depends on the action of the rays on a photographic plate, while certain optical effects are sometimes employed, e.g. the emission of light when the rays fall on a crystal of zinc sulphide. The mass, charge, and velocity of the electrons can be determined by measurements of the quantity of electricity given to a conductor by a stream of the rays and of the extent to which the rays are deviated by known electrostatic and electromagnetic fields. The mass varies with the velocity of the electron.] This was predicted theoretically by J. J. Thomson in 1881 and twenty years later was verified experimentally by Kauffman, who worked with cathode rays. [He found that as the velocity of the rays approached that of light the mass increased continually. The increased value is spoken of as the apparent mass of an electron. The variation in mass with velocity is accounted for by the interaction of a moving charge with the ether.<sup>1</sup>]

<sup>1</sup> The theory of Relativity, which occupies a prominent position in modern physics, gives a general relationship between the mass of any charged particle and its velocity. In practice, however, the variation

A current of electrons is electricity in motion, and a stream of electrons does, in fact, behave in every way like an electric current. Thus it is deflected by a magnet according to the well-known Ampere's rule, just as if it were a wire carrying a current. Similarly a stream of electrons which passes between two charged plates is deflected by the electrostatic field. The extent of the deflection depends upon the mass, charge, and velocity, and increases as the charge increases and the mass and velocity decrease.

### *The Track of an Electron*

Wilson has worked out a method of making visible the path of electrons and other similar charged particles. He uses a "cloud-chamber," which is a vessel containing air and saturated water vapour. By suddenly expanding the air it is cooled and becomes supersaturated with vapour which will condense on any "nuclei" which may be present in the chamber. These nuclei may consist of particles of dust or smoke, or any kind of electrically charged particles, e.g. the gaseous ions which are left along the path of an electron. Hence water condensed on these ions in small drops will form lines and points of mist which can, if suitably illuminated, be permanently recorded by photography. (See Fig. 13, p. 38.) This important method has many applications and can be used to count the number of nuclei (ions) present. The total weight of water condensed can be calculated from the expansion. If the rate at which the cloud of drops falls vertically is observed then from this velocity we can calculate the average diameter of the drops by a relation given by Stokes. From this and the total weight of water in the cloud we can obtain the total number of drops or nuclei.

### *The Mass and Charge of the Electron*

The mass of an electron is only  $\frac{1}{1800}$  part of the mass of a hydrogen atom. The electron has therefore such an extraordinarily small atomic weight that it stands in quite a different class to the ordinary elements. The radius of an electron is in mass only becomes appreciable when the velocity of the particle approaches that of light.

of the order of  $10^{-13}$  cm., i.e. very much less than that of most atoms, namely  $10^{-8}$  cm. In size a hydrogen atom bears the same ratio to an electron as does the earth to the dome of a cathedral. The charge on an electron, or the elementary unit of electricity has been determined by a number of different methods, and is found to be  $1.56 \times 10^{-20}$  electromagnetic units, a value which agrees exactly with that calculated by Planck. It is exactly equal to the charge carried by a monovalent negative ion, e.g.  $\text{Cl}'$ . [An electron is often described as a free elementary unit of electricity. A knowledge of the size of this unit enables us to calculate the number of molecules in a gram-molecule. For example, a chlorine ion carries  $1.56 \times 10^{-20}$  absolute units of electricity and a gram-ion of chlorine ions is found to carry 9,650 such units (96,500 coulombs). Hence a gram ion of chlorine contains  $6.06 \times 10^{23}$  individual ions, and this must also be the number of molecules in a gram-molecule of a chloride, e.g. sodium chloride.] This number<sup>1</sup> is a multiple of Loschmidt's number, or the number of molecules in 1 c.c. of a gas. The values found for Loschmidt's number by the different methods already referred to are exactly in agreement with the value calculated from the charge on an electron.

### *The Production of Electrons*

[Electrons can be produced in many ways. They are a component part of the chemical atom, and can be separated by heat, by light of short wave-length, and by electrical forces. Electrons are also set free in the phenomena of fluorescence and phosphorescence and in the disintegration of the atoms of radioactive substances. In the latter case the residue of the atom carries a positive charge and becomes a positive ion.] Electrons are liberated in many chemical reactions, particularly those which take place at higher temperatures, e.g. in the bunsen flame. [In 1911, Haber and Just showed that this may also occur at lower temperatures when a violent reaction takes place between two chemical substances containing loosely-bound electrons. Thus the action of hydrochloric acid gas, bromine vapour, and phosgene on the liquid alloy of

<sup>1</sup> The number of molecules in a gram-molecule ( $6.06 \cdot 10^{23}$ ) is often termed Avogadro's number.

sodium and potassium was found to be accompanied by the emission of free electrons. The force with which the electrons are held in the atom is measured by the electromotive force required to remove them, or what is termed the "ionisation potential."

### *Ions*

An electrically neutral particle, e.g. a neutral atom or molecule, becomes negatively charged if it takes up electrons and positively charged if it loses them. Such electrically charged atoms or groups of atoms are termed "ions" in accordance with the nomenclature suggested by Faraday. The ions which are concerned in electrolysis are usually written  $\text{Cl}'$ ,  $\text{SO}_4''$ ,  $\text{Cu}'$ ,  $\text{Cu}''$ , the signs ' and ' indicating one negative and positive unit charge respectively. Most of the fundamental work on the phenomena of electrolysis was carried out without any inquiry as to the nature of electricity and the theory of electrons was a later development.

### *Canal Rays*

The canal rays are ions travelling with a high velocity which were discovered by Goldstein in 1886. If a small canal or opening is pierced through the cathode of a cathode ray bulb, these rays are found emerging from it. They are formed along with the cathode rays when electricity is passed through a rarefied gas, and have been studied by precisely similar methods. The canal rays are often found to carry a multiple charge of two or more positive units, but they always carry a whole number of units. Their mass is much greater than that of an electron, and is of the same order as that of the commoner atoms and molecules. Canal rays are in reality identical with the ions of electrolysis, the chief differences being due to their comparatively high velocity and the facility with which gaseous ions acquire multiple charges which are not observed in electrolytic phenomena. Thus, while the ion  $\text{H}'$  is found in solutions of acids, the negative hydrogen ion  $\text{H}'$  has been observed in gases, although it is unknown to the electrochemist. Amongst gaseous ions of this kind the ions  $\text{O}'$  and  $\text{O}'$ ,  $\text{C}'$  and  $\text{C}'$ ,  $\text{C}''$ ,  $\text{C}_2'$ ,  $\text{C}_2'$  have been detected, and even an ion carrying eight positive charges  $\text{Hg}^{++++}$ . The number

of possible compounds of the ordinary chemical atoms with electrons is therefore much larger than one would have expected from the older standpoint of the electrochemistry of solutions.

### *The Quantum Theory*

These physical questions are intimately connected with a theory known as the "Quantum Theory," which was developed by Planck in 1900 to account for certain results obtained by the investigations of radiant heat. It was found that the accepted laws of energy did not hold for rapid vibrations which take part in the phenomena of light and heat.<sup>1</sup> The energy of such vibrations is not continuous, and cannot be exchanged in any amount, however small, but is only emitted in definite "quanta." The size of these quanta depends upon the vibration numbers or frequency ( $\nu$ ) of the vibrating system which is emitting energy and is equal to a simple multiple of  $6.5 \times 10^{-27}$  ergs. The energy quantum is therefore proportional to the frequency. Some values for the energy quantum are given in the following table.

	Red light.	Ultra-violet light.	Röntgen rays.
Wave-length	760 $\mu\mu$	100 $\mu\mu$	0.1 $\mu\mu$
Frequency .	$0.04 \times 10^{16}$	$0.3 \times 10^{16}$	$300 \times 10^{16}$
Energy quantum	$0.26 \times 10^{-11}$ erg.	$195 \times 10^{-11}$ erg.	$19,500 \times 10^{-11}$ erg.

Planck's constant,  $6.5 \times 10^{-27}$  erg/sec. is by far the smallest natural constant which has yet been determined experimentally. It is a most important constant and can be determined in several different ways since it is concerned in many different types of phenomena. Its precise significance is not yet understood; one can only say that energy does behave in what one might almost term an atomic manner. In spite of this, however, the Quantum Theory has been rapidly developed and applied to many branches of physical science.

<sup>1</sup>The Quantum Theory is true both for rapid and slow vibrations. It only becomes of practical importance, however, for higher frequencies when the energy quantum attains an appreciable size.



## CHAPTER IV

### RADIOCHEMISTRY

THE chief contribution of chemistry to our knowledge of the structure of matter is contained in the new science of radiochemistry. Its origin can be traced back to the discovery of Röntgen rays, and the course of its development is so familiar to chemists that we need here only describe briefly the most important results which have been obtained in this field.

#### *Radioactivity*

The discovery of Röntgen rays was followed by a search for other similar rays and finally Becquerel discovered the radiations emitted by uranium. Shortly afterwards M. and Mme. Curie and many other workers found that other elements, e.g. polonium, radium, actinium, etc., possessed this property of radioactivity in a greater or less degree. [Radioactive substances exhibit

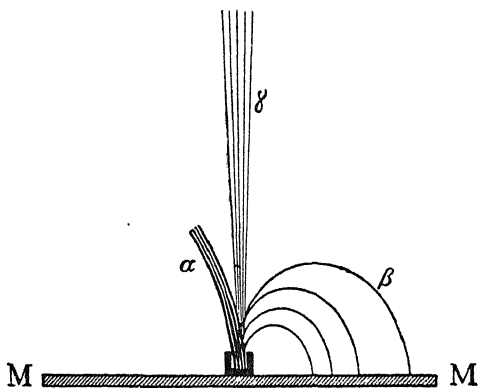


Fig. 12.

a number of characteristic properties. They ionize air and other gases, can bring about certain chemical reactions and affect a photographic plate, cause certain substances to fluoresce, and are always giving out heat. These pro-

perties are due to the emission of a number of peculiar radiations which are affected in a characteristic manner by a magnet and are named the  $\alpha$ ,  $\beta$ , and  $\gamma$  rays. Fig. 12 shows diagrammatically the directions in which these rays are deflected by a powerful magnet MM. The  $\alpha$  rays are bent with difficulty in one direction, the  $\beta$  rays easily in the opposite direction while the  $\gamma$  rays are unaffected.]

### *Disintegration Theory*

The continuous evolution of energy from radioactive substances demanded an explanation which was supplied in 1902 by the well-known theory of the disintegration of atoms, which is usually associated with the names of Rutherford and Soddy but which was partly anticipated by the work of other investigators, e.g. Elster and Geitel. In this theory it is assumed that the atoms decompose but the decomposition is of a type which differs from all chemical phenomena previously known in which unaltered atoms take part. It is accompanied by an energy change a million times greater than that observed in ordinary chemical reactions. The velocity of atomic decomposition follows a very simple law; in a given time interval a constant fraction of the atoms of the radioactive element disintegrate. This may be expressed by the equation

$$N_t = N_0 e^{-\lambda t}$$

where  $N_0$  is the number of atoms originally present,  $N_t$  the number present after a time  $t$ , and  $e$  is the base of the natural logarithms.  $\lambda$  is a constant which has a characteristic value for each radio element. It represents the fraction of the atoms of the element which decompose in unit time. For example, if  $\lambda = 0.0282$  (time interval 1 day) then each day 282 atoms out of 10,000 disintegrate.

When an atom breaks up it forms an atom of another element and in addition  $\alpha$ ,  $\beta$ , or  $\gamma$  rays. These rays have been studied by the methods already referred to (p. 29). The most important properties of these rays are described below.

#### *$\alpha$ Rays*

The  $\alpha$  rays are helium ions carrying two positive charges, and are expelled by a violent disintegration of the atom at a

very high velocity, up to one-tenth that of light. They are therefore closely akin to canal rays. By far the greater part of the energy given out by a radioactive substance is associated with these rays. Their mass  $m$  is 4, or the atomic weight of helium, the mass of the hydrogen atom being taken as unit. The great kinetic energy of the  $\alpha$  rays is due to their high velocity so that the kinetic energy  $\frac{1}{2}mv^2$  ( $v$  = velocity), which is proportional to the square of the velocity, becomes very large. The way in which kinetic energy increases with velocity may be illustrated by the following example. The bullet of the service rifle cartridge weighs about 8 gms., and is expelled with a velocity of 1,000 metres/sec. If its speed were raised to that of an  $\alpha$  particle, 20,000 kilometres/sec., its kinetic energy would be equal to that of a shell of 3,200 tons weight fired at the original speed of 1,000 metres/sec. [The  $\alpha$  rays affect a photographic plate, cause certain substances, e.g. zinc sulphide, barium platinocyanide, etc., to emit light, and ionize gases, making them conductors of electricity. The fluorescence of zinc sulphide excited by radioactive substances has found a practical application in the manufacture of luminous clocks, paints, etc. If one of these luminous objects is examined in a dark room with a powerful lens when the eye has rested a while flashes of light will be seen, each of which is due to the impact of a single  $\alpha$  particle. The ionization of air is brought about by the splitting up into electrically charged ions of a large number (over 100,000) of the atoms and molecules which lie along the track of the  $\alpha$  particle. These ions are attracted by a charged conductor, e.g. an electroscope, and neutralize its charge.]

When  $\alpha$  rays pass through matter, they are slowed down and absorbed. When their velocity is reduced to a certain still large value, about 3 per cent. of that of light, or 10,000 kilometres/sec. in some remarkable and unexplained manner they disappear, and can no longer be detected. This retardation is brought about by a sheet of paper, by 0.02 mm. of aluminium, or by several centimetres of air. They must, of course, give finally helium, but in such small amounts that it cannot usually be detected.

Rutherford and Royds showed conclusively in 1909 that  $\alpha$  rays are chemically identical with helium. They enclosed a

quantity of radium in a glass tube which was so thin (less than 1/100 mm.) that  $\alpha$  rays could pass through its walls, which were still impermeable to ordinary helium. This tube was placed in an outer vessel, which was evacuated, and after a few days helium could readily be detected spectroscopically in the outer vessel. Most of the helium atoms were ejected with such a high velocity that they embedded themselves in the walls of the outer vessel; this helium was set free when the outer was crushed to powder and heated in a vacuum. This experiment accounts for the occurrence of helium occluded in many minerals. Thus 1 gm. of powdered thorium heated in a vacuum gives up 9 c.c. of helium. The helium atoms embedded in the thorium are the remains of  $\alpha$  rays which have been given out for millions of years by disintegrating atoms and which could not escape until the mineral was heated.

The charge carried by an  $\alpha$  particle has been found by different methods, to be two positive units of electricity. Regener measured this charge in the following manner. He determined the number of particles in a weak beam of  $\alpha$  rays by counting the number of flashes in unit time, which were produced when the beam fell on a thin slip of diamond. The charge per particle was then obtained by dividing this number into the total charge carried by the beam, which was measured by an electrometer.

The path traced by  $\alpha$  particles in a gas can be observed and photographed by Wilson's method, described on p. 30. Each particle leaves behind it a large number of ionized gas molecules which act as nuclei for the deposition of water, and so form a line of mist. Fig. 13 is a photograph of the tracks of  $\alpha$  particles obtained in this way; it will be seen that after a certain length of path has been traversed, the  $\alpha$  particle is slowed down and disappears. In some cases the particles are seen to be deflected from their original line of flight; this deflection can be accounted for by the action of the atoms through which the  $\alpha$  particle has passed. In some cases a deflection through a large angle (over  $90^\circ$ ) takes place, which Rutherford explains by the strong forces of repulsion which will be exerted when an  $\alpha$  particle happens to come very close to the positively charged nucleus of an atom.

*$\beta$  Rays*

The  $\beta$  rays are identical with cathode rays, i.e. they are rapidly moving electrons carrying unit electrical charge, and have a mass  $1/1800$ th of that of a hydrogen atom.<sup>1</sup> These rays are expelled from the atom with an extraordinarily high velocity which varies in different cases from 0.3 to 0.99 times the velocity of light. This expulsion of particles with

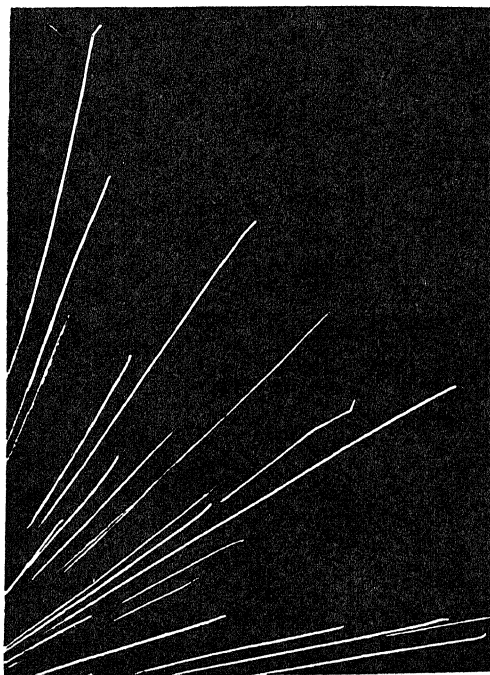


Fig. 13.

such a great velocity is another characteristic property which differentiates radioactive processes from all the chemical and physical reactions previously known, including even the most violent explosions.  $\beta$  rays moving with smaller velocities are produced when rays pass through matter, but are not of much importance.] They have been named by J. J. Thomson  $\delta$  rays.

 *$\gamma$  Rays*

The  $\gamma$  rays are essentially Röntgen rays and are therefore the only one of the three types which really are radiation in Huyghen's sense of the term. They are not material particles like the  $\alpha$  and  $\beta$  rays, which are essentially different from light and can only be termed "rays" in the same sense as that in

<sup>1</sup> This is the mass of rays of small velocity; rays moving with a velocity 99 per cent. that of light have eight times this mass.

which the word might be used to describe the jets of water from a fountain.  $\gamma$  rays are probably a secondary phenomenon of radioactivity; they have a very high frequency and consequently are very penetrating. They are only reduced to half their original intensity by 115 metres of air and are not completely absorbed after passing through 30 cm. of iron. It is the  $\gamma$  rays which are effective in the application of radioactive substance in medicine; one might therefore regard a radioactive preparation as a small and convenient kind of Röntgen bulb.

If a radioactive substance is insulated it usually acquires an electric charge, owing to the loss of  $\alpha$  or  $\beta$  rays. Under ordinary conditions this charge rapidly disappears and is neutralized by the loss or gain of electrons from surrounding objects. In 1909 it was found by O. Hahn that the residue of the atom left when an  $\alpha$  or  $\beta$  particle is expelled recoils like a gun and acquires a considerable velocity. This recoil of the atom has been used to separate and purify many of the radioelements.

### *The Methods of Radiochemistry*

The development of radiochemistry has been facilitated by the working out of a number of new and very delicate methods of investigation. [All the radioelements are very rare and expensive and only a few of them can be obtained in sufficient amounts to be seen and handled like ordinary chemical substances.] Many of them, indeed, are so unstable that they only exist in very small traces, which are not even large enough to be detected by the spectroscope. Hence radiochemistry is largely a chemistry of the invisible. It is only in a very few cases that one of these elements can be characterized by its chemical or physical constants, e.g. melting point, density, etc. [Instead of these the radiochemist uses the "radioactive constant," the "half-value period," the "range" of the  $\alpha$  rays, or the kind of rays which the substance emits. The "range" is measured in cms. of air at 15° C. and 760 mm. pressure; a range of 4 cm. means that after passing through 4 cm. of air the  $\alpha$  particles disappear and can no longer be detected. The  $\alpha$  particles from each radioelement have a characteristic range, which varies from  $2\frac{1}{2}$  to  $8\frac{1}{2}$  cm. in different cases; the range is proportional to the cube of the velocity

with which the particles are initially expelled. The rate of disintegration varies greatly for different elements, and is expressed by the "half-value period" (often shortened to "period"), which is the time in which a given amount of the element would be half disintegrated. The period of a radioelement is a characteristic constant, and is the same at all temperatures and in all compounds of a particular element. Thus radium, whether in the free state or combined to form its chloride, sulphate, etc., always disintegrates with precisely the same velocity. The "half-value period" and the "radioactive constant," are simply related to one another. In the formula

$$N_t = N_0 e^{-\lambda t}$$

where  $N_0$  is the number of atoms at a time  $0$ , and  $N_t$  the number after time  $t$ , let  $N_0 = 1$  and  $N_t = \frac{1}{2}$ . Then  $e^{-\lambda t} = \frac{1}{2}$  or  $t = 0.69315/\lambda$ . This value of  $t$  is the half-value period and varies from  $10^{-11}$  secs. to millions of years for different radioelements.

Methods of measuring these constants with very small amounts of a radioactive substance were worked out and the development of radiochemistry thus became possible. These methods are so delicate that spectrum analysis appears quite crude by comparison; this great sensitiveness is attained in some cases by taking advantage of the fact that very small quantities of electricity can be measured with great accuracy, in others the large kinetic energy possessed by the  $\alpha$  particles is utilized. It has already been mentioned that a single  $\alpha$  particle weighing only  $6.5 \times 10^{-24}$  gm. can be detected by the flash of light which it produces on impact with a crystal of zinc sulphide.]

### *The Radioelements*

[There are thirty-five radioelements or elements in which disintegration of the atom is definitely known to take place. In addition to these, the elements potassium and rubidium emit  $\beta$  rays, but no evidence of other products of disintegration products have been obtained. With the exception of these two elements, the radioactive elements all fall into one or other of two disintegration series which are known as the uranium and thorium families.] The table on p. 41 shows the

Uranium Radium Family	T	Rays.	Actinium Family.	T	Rays.	Thorium Family.	T	Rays
Uranium I   Uranium X <sub>1</sub>   Uranium X <sub>2</sub>   Uranium II   Uranium Y   Protoactinium	5·10 <sup>8a</sup> 23·5 <sup>d</sup> 66 <sup>s</sup> ca. 2·10 <sup>8a</sup> ca. 25·5 <sup>h</sup>	$\alpha$ $\beta$ $\beta\gamma$ $\alpha$ $\beta$	$\rightarrow$ Protoactinium   Actinium   Radioactinium   Actinium X   Actinium Emanation   Actinium A   Actinium B   Actinium C   Actinium C'   Actinium C'   Actinium D	? ca. 20 <sup>s</sup> 18·9 <sup>d</sup> 11·4 <sup>d</sup> 3·9 <sup>s</sup> 0·002 <sup>s</sup> 36·1 <sup>m</sup> 2·15 <sup>m</sup> 4·71 <sup>m</sup> 0·003 <sup>s</sup>	$\alpha$ ? $\alpha\beta\gamma$ $\alpha$ $\alpha$ $\alpha$ $\beta\gamma$ $\alpha\beta$ $\beta\gamma$ $\alpha$	Thorium   Mesothorium I   Mesothorium II   Radiothorium   Thorium X   Thorium Emanation   Thorium A   Thorium B   Thorium C   Thorium C''   Thorium C'   Thorium	ca. 1·8·10 <sup>10a</sup> 6·7 <sup>a</sup> 6·2 <sup>h</sup> 1·9 <sup>a</sup> 3·64 <sup>d</sup> 54·5 <sup>s</sup> 0·14 <sup>s</sup> 10·6 <sup>h</sup> 60·4 <sup>m</sup> 3·1 <sup>m</sup> 10 <sup>-11s</sup>	$\alpha$ ? $\beta\gamma$ $\alpha\beta$ $\alpha$ $\alpha$ $\alpha$ $\beta\gamma$ $\alpha\beta$ $\beta\gamma$ $\alpha$
Ionium   Radium   Radium Emanation   Radium A   Radium B   Radium C   Radium C''   Radium C'   Radium D   Radium E   Radium F (Polonium)   Radium G (Lead)	ca. 10 <sup>8a</sup> 1580 <sup>a</sup> 3·85 <sup>d</sup> 3·05 <sup>m</sup> 26·8 <sup>m</sup> 19·6 <sup>m</sup> 1·38 <sup>m</sup> ca. 10 <sup>-7a</sup> ca. 16 <sup>a</sup> 4·85 <sup>d</sup> 136 <sup>d</sup>	$\alpha$ $\alpha\beta$ $\alpha$ $\alpha$ $\beta\gamma$ $\alpha\beta\gamma$ $\beta$ $\alpha$ $\beta\gamma$ $\beta\gamma$ $\alpha$						

T = Half value period ; <sup>a</sup> = years ; <sup>d</sup> = days ; <sup>h</sup> = hours ; <sup>m</sup> = minutes ; <sup>s</sup> = seconds.



inter-relationships of the elements in these families as completely as the present state of our knowledge permits. The actinium family is arranged as a branch of the uranium group. The type of radiation emitted and the half-value period of each element are included in the table. From Ur. I with a period of 5,000 million years there is formed Ur.  $X_1$ , period  $23\frac{1}{2}$  days, then Ur.  $X_2$ , period 66 secs., and from this Ur. II, which has a period of two million years. At this point the series branches for Ur. II disintegrates in two ways, 97 per cent. going to ionium, period 100,000 years, and 3 per cent. to Ur. Y of period  $25\frac{1}{2}$  hours. These two products disintegrate further to form in the one case radium, radium emanation, etc., and in the other protoactinium, actinium, etc.

In common with many other branches of chemistry radiochemistry is burdened with an arbitrary and unsystematic nomenclature. The elements which were first studied were named at a time when the genetic connection between them was not foreseen; hence these relations are not, as a rule, indicated by the names of the individual elements.

After a sufficient time has elapsed a radio-element and its disintegration products attain an equilibrium in which each product disintegrates as fast as it is produced from its parent element. When this state is reached all the elements are present in a fixed and definite proportion. Thus radium is produced from uranium by a series of disintegrations and all unaltered uranium minerals are found to contain radium and uranium in the constant proportion of 1 : 3,500,000.

### *Radium*

Radium was the first of the new radioelements to be isolated in the pure state. It was discovered by M. and Mme. Curie as a result of their investigations of the intensity of the radioactivity of a number of minerals and compounds containing uranium. They found that pitchblende from Joachimstal possessed an unusually large activity and by using the activity as an indicator tracked down and isolated small amounts of certain new elements. Radium, for example, was found to be carried down by the barium precipitated as sulphate from a solution of the pitchblende and was separated from this element by repeated fractional crystallization as chloride and

bromide. By this process Mme. Curie in 1899 prepared the first specimen of pure radium chloride. Apart from its radioactivity, the properties of radium are quite normal, its atomic weight was found to be 226, corresponding to a definite position below barium in the periodic table, and, as would be expected, the new element exhibited the characteristic chemical properties of a member of the family of the alkaline earth metals. Radium is a divalent metal, its salts closely resemble those of barium in solubility, etc., it gives an intense red coloration to the bunsen flame and produces a spectrum of the same type as that given by the other members of the calcium group. The free element has been prepared by methods precisely similar to those used for the preparation of barium, namely, by heating the azide, or an amalgam obtained by the electrolysis of a salt. Radium metal has a silver-white colour, melts at  $700^{\circ}\text{C}$ . and reacts vigorously with oxygen and water.]

[Radium possesses an intense radioactivity; its period is 1,580 years, i.e. 1 gram of radium is half disintegrated in 1,580 years, which corresponds to about  $\frac{1}{4}$  of a milligram per year for the first few years.] Each gram of radium gives out 3,000 cals. of heat per day, or about the same amount as is produced by the explosion of 1 gram of electrolytic gas to form water. The intense  $\alpha$  and  $\beta$  rays from radium can bring about many chemical reactions, e.g. the blackening of a photographic plate, the conversion of yellow phosphorus into the red form and of oxygen into ozone, the decomposition of water, and the destruction of organic substances, e.g. the tissue of the body. This latter effect is used for combating certain diseases. The high price of radium salts—a milligram of radium bromide is worth about £30—is due to the fact that the minerals from which it can be extracted in small amounts are themselves comparatively rare.] A ton of pitchblende contains about 0.2 gm. of radium and about four-fifths of this can be isolated by a long and tedious process. The annual production of radium is now about 10–20 gms., most of it being extracted in America. The total amount of this element isolated up to the present time is about 50 gms., and it is estimated that there is not more than 500 gms. of “accessible” radium on the earth’s surface. It has been shown by the very

sensitive methods used by the radiochemist that radium in minute amounts is very widely distributed. The average radium content of the crust of the earth is about 1/1000 milligram per ton, and the total amount of radium in the sea is estimated at 20,000 tons.

### *Radium Emanation*

The products of the disintegration of radium are  $\alpha$  and  $\beta$  rays, and a new radioactive element, radium emanation.<sup>1</sup> Each atom of radium splits up into an  $\alpha$  particle, or an atom of helium and an atom of radium emanation.<sup>2</sup> The emanation has entirely different properties from radium; it belongs to the group of inert gases, boils at  $-65^{\circ}\text{C.}$ , melts at  $-71^{\circ}\text{C.}$ , is monatomic, and has a characteristic spectrum. Like the other members of this group it does not form any compounds with other elements. The atomic weight of the emanation can be calculated by subtracting four, the atomic weight of helium from the atomic weight of radium, 226, and should therefore be 222. Ramsay and Gray measured the density of this gas by means of a special type of micro-balance, which was sensitive enough to give sufficiently accurate results with the small amount of emanation—a fraction of a cubic millimetre—which could be isolated from their specimen of radium. In accordance with the calculated atomic weight they found the density to be  $\frac{223}{2}$  times that of hydrogen. Radium

emanation disintegrates rapidly; it is therefore intensely radioactive and, in the liquid state, emits a bright, phosphorescent light. The feeble radioactivity of the water from many wells and springs is due to the presence of dissolved emanation.

A series of products is formed by the disintegration of radium emanation, the last of these being lead. At this stage radioactivity, and hence atomic disintegration, can be no longer detected; lead is therefore regarded as the end product of the uranium family.

<sup>1</sup> The name Niton was given to this element by Ramsay but has not been generally adopted.

<sup>2</sup> Here, and in similar cases, one should use the term "ion" instead of "atom." It is only when the ions have lost their electrical charge that they exhibit the properties of neutral atoms

*Mesothorium*

We need not discuss here the thorium and actinium families, but one member of the thorium family should be mentioned because of its technical importance. This is mesothorium, which possesses an intense activity and has many applications in therapeutics. This element is obtained from the residues left after the extraction of thorium from monazite, etc., and, since these minerals always contain uranium, the mesothorium is mixed with about 25 per cent. of radium. Before the war the annual consumption of monazite sand in the thorium industry was about 3,500 tons; each ton of this sand yields, however, only as much mesothorium as corresponds to an activity equal to that of  $2\frac{1}{2}$  milligrams of radium. The period of mesothorium is 6.7 years, hence it disintegrates much more rapidly than radium. This is the cause of an interesting change in the activity of mesothorium preparations with increasing age. A freshly prepared specimen slowly increases in activity and after three years reaches a maximum value; after this time the activity continually diminishes. It is equal to that of the fresh specimen in ten years, in twenty years it has half this value, and after a still longer period becomes constant at a value depending upon the radium content since the mesothorium has by that time almost completely disintegrated.

Only ten out of the thirty-five known radioelements are stable enough to be isolated in weighable amounts.

*The Radioelements and the Periodic System*

The study of the two series of disintegration products bestowed upon chemistry a large number of new elements which were for some time viewed with great suspicion, since it seemed impossible to find a place for all of them in the periodic system. This difficulty was overcome by the remarkable discovery that several radioelements, in spite of their different atomic weights, had identical chemical properties. Judged only from the point of view of their chemical reactions, they would all be regarded as one and the same element, occupying one place in the periodic table. One pair of such elements is formed by radium and mesothorium. These elements are produced by the disintegration of different elements, they

are isolated from different minerals by different reactions, each has its own characteristic period and atomic weight, their disintegration products have different radioactive and chemical properties, yet in all their chemical reactions radium and mesothorium are identical, and if they are mixed together cannot be separated by any chemical process whatever. The same phenomenon is observed with several other groups of elements. Such elements, which are chemically identical and occupy only one place in the periodic table, are known as "isotopes" (*ἴσος, τόπος*). A group of isotopes is known as a "pleiad," after the best known cluster of stars, while the element in a pleiad which has the longest life is spoken of as the typical element.

The table on p. 47 shows how all the radioactive elements, grouped into pleiads, find a place in the periodic system. It will be seen that the radioactive elements all have a high atomic weight and are therefore made up of atoms with a complicated structure.

### *Displacement Law*

There is a very simple law connecting the type of radiation ( $\alpha$  or  $\beta$  rays) emitted by an element, and the relative positions of the element and its disintegration product in the periodic system. This is the Displacement Law, discovered in 1913 by Soddy, Fajans, and others. If an  $\alpha$  particle is ejected, i.e. an atom of helium with two positive charges, then the new element produced occupies a place two spaces back in the table, or has an atomic number two units lower than that of the parent element. The loss of a  $\beta$  particle gives an element which fills the next space forward in the table, i.e. the atomic number increases by unity. These two rules may be combined into one, namely, that the atomic number changes in the same direction and by the same number of units as does the positive electrical charge on the atom. Here we have revealed the physical significance of the atomic numbers. We have already seen that there must be some physical constant of an atom which changes by equal amounts from element to element in the table, as demanded by Moseley's Law of High Frequency spectra. This constant can be nothing else than electrical charge. It is this which fixes the position of the elements in

# THE POSITION OF THE RADIOELEMENTS IN THE PERIODIC SYSTEM

[illegible]

a series which, since it was first recognized by the periodicity of chemical properties, has hitherto been named the periodic system.

The disintegration of an atom may or may not involve a change in atomic weight. If a  $\beta$  particle is ejected, there is practically no change, since the mass of an electron is so small ( $1/1,800$  of the mass of an hydrogen atom); the loss of an  $\alpha$  particle produces an element with an atomic weight 4 units less than that of the parent element corresponding to the loss of one atom of helium.

### *Disintegration of Uranium*

Thus, for example, the disintegration of uranium proceeds according to the following scheme :

$U^1$  (Uranium, VI, 238)  $\rightarrow$   $UX^1$  (Thorium, IV, 234)  $\rightarrow$   $UX_2$  (Protoactinium, V, 234)  $\rightarrow$   $U_2$  (Uranium, VI, 234)  $\rightarrow$  Io (Thorium, IV, 230)  $\rightarrow$  Ra (Radium, II, 226)  $\rightarrow$  RaEm (Radium Emanation, O, 222)  $\rightarrow$  RaA (Radium F or Polonium, VI, 218)  $\rightarrow$  RaB (Lead, IV, 214)  $\rightarrow$  RaC (Bismuth, V, 214)  $\rightarrow$  RaC' (Polonium, VI, 214)  $\rightarrow$  RaD (Lead, IV, 210)  $\rightarrow$  RaE (Bismuth, V, 210)  $\rightarrow$  RaF (Polonium, VI, 210)  $\rightarrow$  RaG (Lead, IV, 206).

This table gives first the symbol of the element, then the typical element with which it is chemically identical, then the number of the group in the periodic system to which it belongs, then its atomic weight, and finally the type of radiation emitted on further disintegration. It will be seen that elements of different atomic weight can be chemically identical, e.g. RaB, 214, RaD, 210, RaG, 206, in the lead pleiad ; or elements with the same atomic weight may have different chemical properties, as is shown by the elements RaD (typical element Lead), RaE (Bismuth), and RaF (Polonium), which all have an atomic weight of 210.

Statements of this kind do violence to our long-established notions about the nature of elements, and unless one has followed carefully the development of radiochemistry, one might well regard them as an instance of the too exuberant imagination of the radiologist. Yet all of them are based upon unimpeachable experiments. Thus, in the case of the isotopes of lead, one would expect that the lead formed by the disintegration of uranium would have a smaller atomic weight (206)

than that of common lead, which from a number of accurate determinations is known to be 207.19. The value for the uranium lead can be calculated from the atomic weights of uranium or radium by subtracting the weight of the particles lost by disintegration.

$$\text{Uranium } 232.18 - 32.00 \text{ (8 helium atoms)} = 206.18$$

Radium  $225.96 - 20.00 (5 \quad , \quad , ) = 206.07$

Richards, Honigschmid and others have determined accurately the atomic weight of specimens of lead extracted in small amounts from very pure uranium minerals, e.g. the pitchblende from Morogovo in East Africa, and have found it to be 206.08 in excellent agreement with the calculated value. This work and the further study of the isotopes of lead have provided a firm experimental basis for the theory of isotopes. In spite of this appreciable difference in atomic weight the lead isotopes have exactly the same chemical properties, the same spectrum (with the exception of a very small difference in the wave-length of one line), the same Röntgen ray spectrum and the same melting point, etc. It is only in those properties which depend upon the atomic weight of the element or the molecular weight of a compound that any difference is found. Thus the densities of the metals differ in the same ratio as their atomic weights.

		Atomic weight.	Density.	Atomic Volume.
Common lead	. .	207.19	11.337	18.277
Uranium lead	. .	206.08	11.273	18.281

There is a similar difference in the specific solubilities of the salts which is just the difference necessary to make the molecular solubilities identical.

Another isotope of lead, which should have a higher atomic weight than common lead, occurs in the thorium family, and Honigschmid has, in fact, found the atomic weight of lead extracted from thorium minerals is 207.90. Thus a range of atomic weights differing by nearly 1 per cent. has been experimentally established for the lead isotopes.

Still another case in which the theory has been verified is that of thorium and ionium. Thorium has an atomic weight of 232.15, while that of ionium is calculated to be 230; a



specimen of thorium chemically pure, but which from radioactive evidence was known to contain ionium, gave an atomic weight of 231.5.

### *The Significance of Radiochemistry*

Our discussion of radiochemistry must end here, but enough has been said to make it clear that this science has led to results which are of the greatest significance for many other branches of knowledge. Thus it has given us a much clearer conception of the structure of matter and has finally settled the long dispute as to the possibility of the transmutation of elements. It is no longer possible to retain the older view that the atoms of the elements are the smallest constituent particles of matter ; we can now only regard them as particles which are extraordinarily resistant to chemical forces. Radiochemistry has made clear the essential meaning of the periodic system. It has further thrown a great deal of light on many of the problems of geology and astronomy. For instance it has given us a method of determining the age of minerals. A gram of thorianite is found to contain 9 c.c. of helium gas ; from the thorium content of this mineral it can be calculated that only  $3.7 \times 10^{-8}$  c.c. of this gas are produced annually, hence at least 240 million years must have elapsed since this mineral was first formed—or rather since the portion of the earth's crust in which it is found first reached the solid state. The energy set free by atomic disintegration introduces a new and hitherto neglected factor into the heat balance of the planets which, for example, falsifies all the older calculations of the age of the earth based on its rate of cooling. According to Svedburg, an average radium content of  $2 \times 10^{-9}$  gms. per cubic metre would, by its disintegration, give out enough heat to balance the loss by radiation, etc. ; the rocks and minerals of the earth's crust which have been investigated show that the average radium content is probably greater than this amount.

### *The Future of Radiochemistry*

How much farther will radiochemistry yet go ? The dream of the alchemist of converting lead into gold does not seem so

ludicrous to-day as it did two hundred years ago, and we may one day be able to initiate and control the disintegration of elements. If this can be done a tremendous amount of energy will be set free. A gram of radium disintegrated completely into helium and electrons would develop  $10^{11}$  cals., a quantity a million times that developed by the most violent chemical reaction hitherto observed. If this energy could be utilized it would form by far the most important source of power for industrial purposes.

### *Disintegration of Inactive Elements*

The answer to these questions must be left to the future. Another problem intimately connected with them is the nature of the inactive elements. Do the radioelements form a class apart and are the atoms of the other elements unalterable? We cannot believe that there are two such essentially different classes of atoms. [The elements potassium and rubidium which give off  $\beta$  rays are probably an intermediate stage between the radioelements and the commoner atoms.] It must not be forgotten that we can only detect the disintegration of an atom when it is accompanied by certain intense and characteristic phenomena which we term radioactivity. Probably all that is required to trace experimentally a genetic connection between the non-radioactive elements is a refinement of our instruments or the discovery of new methods of attacking the problem. It is certain from the very careful chemical work which has been carried out on these elements that they are very stable, much more stable than uranium and thorium, which have periods measured in thousands of millions of years. One fact which is significant in connection with this problem is that 99 per cent. of the earth's crust is made up of elements with an atomic weight less than 60. It seems probable that elements of lower atomic weight would be more stable and would disintegrate more slowly than those made up of heavier and more complicated atoms.

It is also worth noting that certain elements are nearly always found in Nature associated with other elements from which, possibly, they are derived. According to the recent work of Aston many elements which were previously thought

to be simple substances are chemically inseparable isotopes.<sup>1</sup> One would therefore expect that the same element from different minerals might contain these isotopes in different proportions and so exhibit variations in atomic weight. These differences have, up to the present, been found only with lead and the radioactive elements. Experiments on American and German copper, on sodium and chlorine from many different sources, on silver and iron from meteorites and terrestrial minerals have all failed to show any difference in atomic weight. The question cannot yet, however, be regarded as settled, especially as it has not hitherto been approached from the point of view of radiochemistry. Hahn has suggested that the atomic weights of certain specimens of calcium and barium may differ from the accepted values for these elements. If the radioactivity of potassium is due to disintegration of its atoms, the loss of a particle would give an isotope of calcium of atomic weight 39. Similarly rubidium may produce an isotope of strontium and caesium which, however, exhibits no detectable activity, may be very slowly converted into an isotope of barium. The atomic weights of these isotopes 39, 85.5, and 132.8, are lower than the commonly accepted values for calcium, strontium, and barium, 40, 87.6, and 137.4. This hypothesis is being tested by the determination of the atomic weight of calcium extracted from certain potassium minerals, e.g. orthoclase. Even if all the tests fail to show differences between the samples of one and the same element obtained from different natural sources, it has been suggested by Richards that this may be due to a thorough mixing of the different isotopes when the earth was in a molten or gaseous state. If this is the case, then only those elements which have been produced subsequently by disintegration would be expected to show differences in atomic weight.

Although mixtures of isotopes behave chemically as a single element, it is possible, by physical methods, to separate and recognize their component elements. For this purpose it is necessary to use those physical phenomena which depend upon the mass of the molecule. Bronstead and Hevesy have partially separated mercury into its isotopes by repeated fractional diffusion, while other investigators have separated hydrochloric

<sup>1</sup> See p. 53.

acid gas into two fractions of slightly different density and molecular weight which contain in different proportions the isotopes of chlorine.

The greatest advance in this field has been made by F. W. Aston, who has developed and extended the work of J. J. Thomson on canal rays. By examining volatile compounds of a number of elements he has been able to decide which of them were composed of only one kind of atoms, or were "pure elements" and which were "mixed elements" made up of several different isotopes. The substances examined were made to form electrically charged canal rays (see p. 32), which were deflected by a magnetic and an electric field. A particle having a mass  $m$ , a charge  $e$ , and a velocity  $v$ , is deflected in an electric field by an amount proportional to  $\frac{mv^2}{e}$ , while the

deflection in a magnetic field is proportional to  $\frac{mv}{e}$ ; from the observed deflections the mass of the particle can be calculated. It was known already from Thomson's work that neon consisted of two isotopes of atomic weights 20 and 22. Aston devised a method of "focussing" or bringing to one point a bundle of canal rays and in this way obtained a very considerable increase in accuracy. His instrument records photographically a "mass-spectrum" containing a number of lines, the position of which depends upon the masses of the particles which produce them. The most important of his results up to the present time are as follows:

With the single exception of hydrogen (at. wt. 1.008), all the elements so far investigated have atomic weights which are exactly whole numbers on the scale  $O = 16$ . The fractional values for some elements, e.g.  $Cl = 35.46$ , are found to be due to the presence of two or more isotopes. The following elements have been shown to be "pure elements." H, He, Be, C, N, O, F, Na, P, As, I, Cs. The "mixed elements" which have been examined are Li (a mixture of isotopes with atomic weights 6 and 7), B (9 and 10), Ne (20, 22, ? 21), Si (28, 29, ? 30), Cl (35, 37, ? 39), A (36, 40), K (39, 41), Ni (58, 60), Br (79, 81), Kr (78, 80, 82, 83, 84, 86), Rb (85, 87), Xe (129, 131, 132, 134, 136, ? 128, ? 130), and Hg (197, 200, 202, 204, etc.). In addition, sulphur is probably a mixed element. It appears that

Prout's hypothesis that the atomic weights of the elements are whole numbers is correct.

Rutherford by bombarding nitrogen with  $\alpha$  rays, has recently obtained a new type of radiation which has a much greater range (28 cms.) than the  $\alpha$  rays which produce it. From the deflection of these rays by electrical and magnetic fields, it is found that they consist of rapidly moving hydrogen ions which have, apparently, been expelled from a nitrogen atom by the impact of an  $\alpha$  ray. In a similar manner hydrogen ions have been "knocked out" of other atoms, e.g. B, Fl, Na, Al and P. No hydrogen particles were produced from C, O, S, and other elements which have atomic weights divisible by 4; it seems probable that these elements are made up entirely of helium and do not contain hydrogen. One remarkable feature of these experiments is the great range of some of the hydrogen ions; those from aluminium have a range of over 80 cms. of air. The kinetic energy of these secondary rays is in many cases greater than that of the  $\alpha$  rays by which they are produced, and this extra energy can only have come from within the decomposing atom. Here, then, we have for the first time an artificial disintegration.

## CHAPTER V

### THE STRUCTURE OF CRYSTALS

WE must now turn our attention to the problem of the structure of crystals. As we have seen already, the methods of Röntgen ray optics have led to great advances in this field.

#### *The Laws of Crystals*

The more recent work confirms the older view that crystals are composed of constituent particles arranged in some definite space-lattice. The different types of crystal lattice may all be supposed to be built up of definitely arranged layers of atoms superimposed according to certain principles of symmetry. The "grating element" of these lattices measures about  $10^{-7}$  to  $10^{-8}$  cms. and the corresponding "crystal element" may be a molecule, an atom, or an electrically charged ion.

In many cases one cannot distinguish molecules in a crystal for apparently the individual atoms are bound in the same way to all their neighbours. It seems probable, however, that the forces which bind crystals together are the same as the ordinary chemical forces between atoms. P. Pfeiffer regards crystals as compounds of very high molecular weight which have a structure in accordance with the laws of co-ordination of the well-known theory of Werner.

Fig. 14 shows the arrangement of sodium and chlorine atoms (indicated by a disc and a circle respectively) in a cubical crystal of common salt. The chlorine and sodium atoms are arranged in exactly the same manner; each sodium atom is surrounded by six chlorine atoms at the corners of an octahedron with the sodium atom at the centre, while each chlorine atom is similarly surrounded by six atoms of sodium. From the most accurate measurements, the side of the "elementary cube" has a length of  $2.814 \times 10^{-8}$  cms. It has been shown, by Debye and Scherrer, that in lithium fluoride, which has a

similar structure, the points on the space lattice are occupied, not by lithium and fluorine atoms, but by the ions  $\text{Li}^+$  and  $\text{F}^-$ , which are formed when this salt is dissolved in water. Such substances are said to have an "ionized" structure. This observation is of great interest and importance, and has led to attempts to correlate many other properties of crystals. It seems to indicate that the forces which hold the atoms together in a crystal are the well-known electrostatic forces

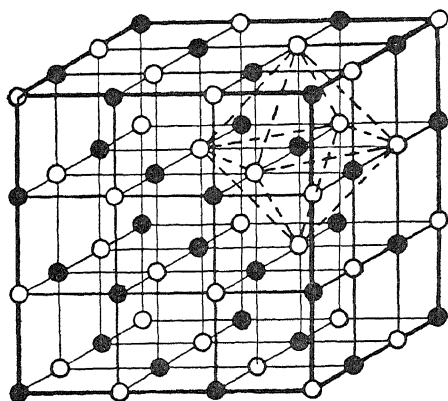


Fig. 14.

of attraction between two bodies carrying charges of opposite sign. From this point of view Born has tried to account for the mechanical properties of crystals in terms of electrical force; by ascribing the elastic resistance of a crystal to these forces he has been able to predict the compressibilities of the halogen compounds

of the alkali metals with results in good agreement with the values found by experiment. The ionization of a salt, e.g. sodium chloride, when dissolved in water, is immediately accounted for if this substance possesses an "ionized" structure, for the ions already exist in the crystal and should be separated easily when the salt is dissolved in a solvent with a high dielectric constant.

At the surface of a crystal these electrical forces will not be completely neutralized and some force may be exerted outwards. This effect has been used as a basis for theories of absorption and surface electrochemical effects.

### *Mixed Crystals*

A mixed crystal, e.g. a crystal containing  $\text{NaCl}$  and  $\text{LiF}$ , does not contain separate molecules of these substances with, say, all the lithium ions adjacent to fluorine ions, but the lithium and sodium ions are spread evenly over the space lattice

and are surrounded by chlorine ions symmetrically interspersed with fluorine ions.

### *Structure of Diamond*

The structure of diamond is based upon a cubical arrangement of the carbon atoms, each of which is surrounded by four other carbon atoms arranged in the form of a tetrahedron. Each atom is therefore bound to four neighbouring atoms by its four valencies. The length of the side of the "elementary cube" is  $3.53 \times 10^{-8}$  cms.

### *Structure of Graphite*

It is interesting to compare the structure of diamond with that of graphite since in crystalline form there is no obvious resemblance between these two forms of carbon. According to the work of Debye and Scherrer, graphite is built up of a number of planes of carbon atoms, each plane being situated at a distance of  $3.41 \times 10^{-8}$  cms. from the next. In each plane the atoms are arranged at the corners of a regular hexagon in a kind of honeycomb structure (see Fig. 15). The side of the hexagon has a length of  $1.45 \times 10^{-8}$  cms. The carbon atoms in adjacent planes are not vertically over one another, but are displaced in such a manner that carbon atoms in alternate planes are in the same vertical line. From each atom three valencies are supposed to radiate at angles of  $120^\circ$  and bind it to its neighbours in the same plane, while the fourth valency is used to bind together the different planes. The greater distance over which these latter valencies have to work should correspond to a weaker union, so that one would expect that it would be easier to cause a relative displacement of the planes than to disturb the atoms held in the network of which the planes consist. This gives an explanation for the ease with which crystals of graphite can be split into thin sheets parallel to the planes of carbon atoms and also for its great compressibility. By applying force in the right direction, it is possible to diminish the distance between the planes of carbon atoms

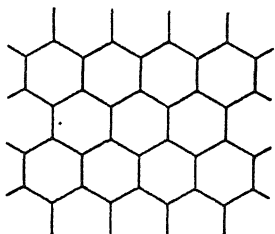
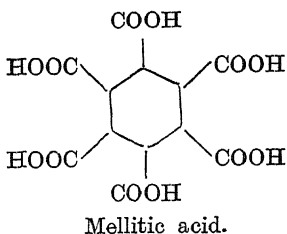


Fig. 15.



by 15 per cent. The use of graphite as a lubricant and for making lead pencils depends upon these properties of softness and elasticity. We see, therefore, that the cleavage plane of a crystal or the plane along which it splits most easily may be regarded as a plane of smallest chemical affinity.

It has also been found by these methods that the so-called amorphous carbon does not differ essentially from graphite in structure and is composed of very small crystalline particles.



From the breadth of the lines obtained in Debye and Scherrer's method it is estimated that in some cases the individual crystals do not contain more than 30 carbon atoms.

The two allotropic forms of carbon have chemical properties which are in harmony with these views of the structure of their crystals. Diamond shows the greater resistance to chemical reagents and has its atoms more tightly bound together. On the other hand, graphite and "amorphous" carbon can be oxidized much more easily and give mellitic acid (benzene hexacarboxylic acid) in which the carbon residue still retains a fragment of the web of atoms in the crystal, the hexagon of the graphite structure being represented by the benzene nucleus.

### *Amorphous Substances*

Many substances which were previously regarded as amorphous exhibit a finely crystalline structure when examined by Röntgen rays. "Amorphous" silicon, for example, has a structure similar to that of diamond, each silicon atom being separated from its neighbour by a distance of  $2.3 \times 10^{-8}$  cms. The same thing is true for a number of colloidal substances; the smallest particles in a solution of colloidal gold, particles too small to be detected even by the ultramicroscope, appear to be small crystalline cubes, whose sides are made up of 4 or 5 atoms of this element. Certain organic substances, e.g. starch and cotton, are also said to give evidence of a crystalline structure when examined by Röntgen rays; this question will shortly be discussed elsewhere and at present the crystalline nature of these substances cannot be regarded as proved.

## CHAPTER VI

### THE STRUCTURE OF ATOMS

WE shall now discuss the structure of the atom itself from the standpoint of the various "atom-models" which the physicist has worked out. In the following pages a number of these models will be described but no attempt will be made to distinguish critically between them.

Atoms are now known to be composed of smaller particles; from radiochemical evidence we can deduce that electrons or  $\beta$  rays and certain atoms of small atomic weight, e.g. the hydrogen and helium ions,  $H^+$  and  $He^+$ , are components of the heavier atoms.

Moseley's law, which stated that the square root of the frequency of the characteristic Röntgen radiations of the elements is proportional to the atomic number, tells us that there must be some characteristic quantity for each atom which changes by equal amounts from atom to atom in an unbroken series over the whole range of the known elements. The displacement law of radiochemistry (see p. 46) shows that this characteristic quantity is the electrical charge on the atom. This positive electrical charge, often described as the nucleus of the atom, increases by equal amounts for each unit of increase in the atomic number; one can go farther and, as Van den Broek suggested in 1913, take the nuclear charge as equal to the atomic number and still retain complete agreement between hypothesis and experiment.

#### *The Nucleus of the Atom*

Rutherford has studied the manner in which positively charged  $\alpha$  particles are deflected when they collide with the atoms of a number of different elements, and has shown that the kind of deflection can only be accounted for by assuming that positive nuclear charge is concentrated in a very small

space only about  $10^{-12}$  to  $10^{-13}$  cms. in diameter. This minute but massive charge is what is known as the nucleus of the atom. The number of positive charges on the nucleus can be calculated from the magnitude of the force with which it repels an  $\alpha$  particle; this number was found by Rutherford to be of the same order of magnitude as the atomic number. The charge referred to here is the "free" positive charge or the number of unit positive charges not neutralized by electrons. We cannot at present determine how many electrons are contained in the nucleus, but the emission of  $\beta$  rays when atoms disintegrate shows that they are certainly present in some atoms. In such atoms the nucleus will contain a number of positive charges equal to the atomic number, and in addition the same number of positive charges as there are electrons in the nucleus.

The weight of an atom in many cases gives further support to the view that the nucleus contains a larger number of positive charges than that represented by the atomic number, assuming that this charge is made up of  $\alpha$  particles. Thus, the atomic number of the heaviest atom, that of uranium, is 92, and this is the number of free positive charges on the nucleus. This number corresponds to 46 double charged helium atoms or  $\alpha$  particles, which have a total mass of only  $4 \times 46 = 184$ , while the atomic weight of uranium is 238. As the mass of the electrons ( $1/1,800$  that of a hydrogen atom) is negligible compared with that of the other particles, we are driven to the conclusion that the nucleus of the uranium atom contains a larger number of the heavier constituents than is represented by 46 helium atoms. For example, one might suppose that the nucleus was made up of 59 helium ions  $\text{He}^{++}$ , 2 hydrogen ions  $\text{H}^{+}$ , and 28 electrons. Its charge would then be  $2 \times 59 + 2 \times 1 - 28 = 92$ , and its mass  $4 \times 59 + 2 \times 1 = 238$ . No special significance should be attached to these numbers. They are purely speculative, and the same remark applies to all the attempts which have been made to define numerically the structure of the nucleus.

#### *Nuclear Charge and the Periodic System*

This conception of atoms gives a new basis for the periodic system which must now be regarded as an arrangement of

the elements in the order of their nuclear charge with a regular increase of one unit of free positive electricity from element to element. The possible number of nuclear charges from hydrogen to uranium is 92 and allows for the existence of 92 chemically distinct elements of which 5 have yet to be discovered.

### *The Electrons in Atoms*

The atom of an element in its normal state is electrically neutral; when it carries an electric charge it is termed an "ion." Hence we must assume that the nucleus of the atom is surrounded by electrons equal in number to the nuclear charge or, what is the same thing, the atomic number. The space occupied by these electrons, or the "Sphere of electrons" is much larger than the volume of the nucleus as found by Rutherford, and is identical with what is usually termed the volume of the atom. From a large number of measurements by different methods it is known that the average diameter of an atom is about  $10^{-8}$  cms.

### *Outer and Inner Electrons*

It is now necessary to draw a distinction between two types of electrons which differ in their position within the atom. These are :—

- (1) the outer electrons which occupy the sphere of electrons and are held comparatively loosely. Some of them at least are detached from the atom or added on to it in many thermal, electrical, and chemical reactions, thus producing charged atoms or ions. A change in the number of outer electrons does not cause any fundamental change in the character of the atom but probably corresponds to a change in valency.
- (2) the inner or nuclear electrons which are very firmly held. They cannot be split off from the atom by any physical or chemical process, but are spontaneously ejected when an atom disintegrates. The loss of one of these electrons leads to a profound disturbance and rearrangement, and a new element with different chemical properties is formed. Such a change, involving the nucleus, is accompanied by the phenomena of

radioactivity and the emission of energy on a very much larger scale than is ever observed with ordinary chemical reactions.

The different radiations which an atom can emit are originated by the moving outer electrons which, according to their position in the atom, may initiate vibrations over a large range of frequencies from the infra-red to Röntgen rays. The vibration of these electrons may be excited by external forces, e.g., heat, light, Röntgen rays, or the impact of electrons (cathode rays), etc.

The forces which hold the outer electrons are the resultant of the attraction of the nucleus and the mutual repulsion of the electrons themselves. Under certain conditions, e.g. in electrolysis, these electrostatic forces can be overcome by an external opposing force, and an electron split off. The amount of energy needed to split off an electron measures the firmness with which it is held in the atom and is known as the "ionization potential." It is obvious that the electrons in the outer regions of the sphere of electrons will be most easily detached while those which are closer to the nucleus will be held much more firmly. In accordance with this the Röntgen rays are associated with the electrons in the immediate neighbourhood of the nucleus. Proceeding outwards from the nucleus the electrons in successive zones are associated with radiations of longer and longer wave-length, first the longer Röntgen rays, then the still unknown rays between the Röntgen rays and the ultra-violet, then the ultra-violet, the visible and the infra-red rays, etc. The outermost electrons which are most easily detached, for example by electrolysis, are known as "valency electrons."

### *Atomic Structure and Atomic Properties*

The relative positions of the electrons in an atom, and therefore the chemical and optical properties of an element, are determined solely by the number of free positive charges on the nucleus. The structure of this nucleus fixes the mass and weight of the atom and also its stability and life-period. The number of free positive charges has nothing whatever to do with the rate of disintegration of the atom which depends

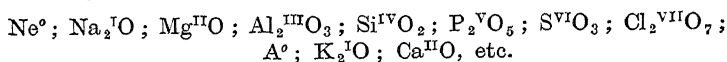
only on the structure of the nucleus. If the nucleus of an atom loses an  $\alpha$  particle, i.e. two positive charges and then two electrons a new element is formed which has the same nuclear charge as the parent element and is chemically identical with it (for instance, the elements uranium I and uranium II). These elements differ in mass (atomic weight) however by four units, and owing to the different structure of the nucleus, have very different rates of disintegration. If the nucleus loses a  $\beta$  particle the number of free positive charges increases by one unit and a new element with different optical and chemical properties but the same atomic weight is produced. The displacement law of radiochemistry can thus be accounted for on this view of the structure of atoms. It will be seen that the mass of an atom or the atomic weight is only of secondary importance in the newer interpretation of the periodic system.

### *Ions and Atoms*

A neutral atom contains a number of electrons surrounding the nucleus exactly equal to the number of free positive charges on the nucleus. If an electron is added, or using the language of chemistry, if the atom combines with more electrons, it becomes negatively charged and is converted into a mono-, di-, or tri-valent negative ion. Similarly the loss of an electron gives a monovalent positive ion. Thus the cupric ion  $\text{Cu}^{++}$ , does not, like the atom of copper, contain 29 outer electrons corresponding to the atomic number of copper, 29, but only 27; it has lost two electrons, and the ion as a whole has two free positive charges. Similarly, the oxygen ion  $\text{O}^{--}$  possesses two more electrons than the eight which correspond to the atomic number of oxygen and is a divalent negative ion. It has long been evident from Faraday's laws of electrolysis that these movements of electrons are intimately connected with chemical forces, and it seems highly probable that chemical reactions are brought about by the exchange of electrons. The inert gases which show no inclination or capacity to form chemical compounds probably are composed of atoms which possess a very stable external system of electrons. In other words, the ionizational potential, or the energy required to detach an electron from the atom of one of these gases is unusually high.

*The Periodic Properties of Atoms*

When the elements are arranged in order of increasing nuclear charge or atomic number it is found that there is a periodic change in chemical properties, in the characteristic radiations emitted by the element, in atomic volume, and in many other properties. This leads at once to the conclusion that there must be a recurrence of similar groupings of the outer electrons on which these properties depend. Elements with the same valency are separated by definite intervals of atomic number. In the first series of the periodic system the positive valency (with respect to negative elements, e.g. oxygen and the halogens) increases by one for each increase of one unit of atomic number which corresponds to one more outer electron. After eight steps of this kind there is a sudden change with one of the inert gases when the valency sinks to 0 and then begins to rise again. This regularity is well seen in the formulae of the highest true oxides (not peroxides) of the second series.



It seems highly probable that the electrons added as the atomic number increases, form loosely held valency electrons and so produce this increase in valency; after a certain number have been added a rearrangement of the outer electrons seems to take place.

While many of the properties of an atom, especially its valency, depend upon the outermost and most loosely held valency electrons, a certain connection can be traced between the arrangement of the electrons nearer the nucleus, and the chemical and physical characteristics of an element. The structure of the whole sphere of the electrons surrounding the nucleus is, of course, determined by the number of free nuclear positive charges. This effect of an increased number of electrons or an increased nuclear charge is seen when one compares the members of a vertical group of the periodic system. The alkali metals, for example, show a great similarity in chemical properties and have the same valency in accordance with the view that they have the same arrangement of their outermost electrons. As the atomic number increases, there is in addition a progressive change in melting

point, boiling point, density, and chemical properties. It is a general rule that the elements of higher atomic number are more strongly electropositive.

While these ideas give us a very useful picture of the structure of atoms there are still many points on which we are completely ignorant. We do not know, for example, whether the forces which hold together the positive charges in the nucleus are identical with electrostatic forces or not, neither can we say what it is that determines the mass of a particular atom. Our knowledge of atomic structure is thus far from complete, and offers many difficult problems to the physicists who are still seeking to unravel the riddle of this microcosm. One of the most important of these problems is the determination of the exact arrangement of the electrons in the outer sphere which occupies by far the greater part of the volume of the atom.

The periodicity of the Röntgen rays in the K, L, and M, series does not coincide with the periodicity of chemical properties. The same type of Röntgen radiation is produced by a series of elements which is longer than, and overlaps the series of the periodic table. From this fact it is argued that a particular grouping of the electrons nearest the nucleus (from which the Röntgen rays originate), may persist over a considerable range of atomic numbers.

#### *Rutherford's Atom-model*

At an earlier stage (1904), J. J. Thomson thought that the positive nucleus of the atom was comparable in size with the volume of the atom and that the electrons moved within this sphere of positive electricity. In 1911 Rutherford's observations on the penetration of atoms by  $\alpha$  and  $\beta$  rays led to the adoption of another view of atom structure. Physicists now regard an atom as consisting chiefly of empty space containing a minute positive nucleus around which still smaller electrons move with a high velocity. An atom is therefore pictured as a kind of "planetary" system.

#### *The Rutherford-Bohr Model of the Hydrogen Atom*

A great advance in physical theory was made in 1913 by the Danish physicist Bohr, who extended Rutherford's theory to



define the orbits in which the electrons move around the nucleus. In the first place Bohr discussed the structure of the simplest atom, that of hydrogen, and developed a theory of its optical properties which successfully accounted for the existence of series of lines in the spectrum of this gas. The next simplest atom, that of the helium ion  $\text{He}^+$ , was discussed in a similar manner.

Bohr's conception of the hydrogen atom was based on the Rutherford type of atom-model and assumed that the atom consisted of a minute positively charged nucleus around which an electron of similar dimensions to the nucleus moves in a circular orbit. The electron need not always be confined to one particular path or velocity, but may occupy one or another of a number of fixed orbits in which it moves with a series of velocities which can be calculated by an application of the Quantum theory. It is assumed that the electron does not emit radiation as long as it remains in any one orbit; it may, however, be displaced from one orbit to another by thermal or electrical impulses, and subsequently return to its original path. When this takes place radiation is supposed to be given out with a particular frequency which depends upon the kinetic energy of electron in its initial and final orbits, and can be calculated by means of the Quantum theory. In the case of the hydrogen atom the radiations produced fall entirely in the visible and ultraviolet regions of the spectrum; the outermost electrons of more complex atoms are responsible for the ordinary radiations and those nearest the nucleus for the characteristic Röntgen rays. It can be shown that the radii of successive stationary orbits of the electron in a hydrogen atom are in the ratio of the squares of the natural numbers, or as 1 : 4 : 9 : 16, etc. Without going more deeply into the mathematics of the subject, it is sufficient to state that on this depends the explanation of the existence of a series of lines in the spectrum of hydrogen which have the wave-lengths defined by Balmer's formula  $\lambda = 3646.13 \frac{m^2}{m^2 - 4}$  (see p. 15),

in which again the squares of the natural numbers are concerned. Bohr's theory of the optical properties of hydrogen gives results which are accurately in agreement with the observed frequencies of the lines in the spectrum of this gas.

Its value was therefore at once appreciated by physicists, who have attempted to apply it in a number of other cases ; it should be mentioned, however, that this theory leads to conclusions about other properties of hydrogen which are by no means in harmony with experiment.

According to Bohr, the first or innermost orbit of the electron in a hydrogen atom has a radius of  $0.55 \times 10^{-8}$  cms., while the next orbit has four times this radius, and so on. The electron travels round this innermost path  $6.2 \times 10^{15}$  times a second, and is therefore moving with a velocity of 2,000 metres per second. If one imagines the hydrogen atom magnified to such a size that the nucleus has a diameter of 10 cms., then the electron would have a diameter of 2 cms. and would move in the innermost orbit at a distance of 1,000 metres from the nucleus. Thus by far the greater part of the hydrogen atom consists of empty space.

#### *The Structure of Other Atoms*

It is generally supposed that other atoms possess a similar structure ; they contain electrons moving in definite orbits about the nucleus, and the emission of radiation is supposed to be connected with the transference of an electron from one orbit to another. As soon, however, as we consider in detail the structure of the next simplest atom to hydrogen, namely helium, we meet with divergences of opinion. Some workers assign separate orbits to the two electrons which are associated with the doubly charged nucleus of helium, others regard them as moving in the same orbit.

Still more divergent views are held with respect to the structure of more complicated atoms, a subject which has offered a very fertile field for speculation. We are as yet too ignorant of the fundamental physical laws of the atom to be able to deduce on physical grounds the detailed arrangement of their electrons. It is necessary to bring in chemical evidence to arrive at a working model of the atom.

It is believed that the nucleus of an atom is surrounded by several rings or shells of electrons. By considering the chemical properties of the elements of lower atomic weight one can arrive at an arrangement of electrons in the separate rings such as that shown in the table below. The first number

represents the number of electrons in the innermost ring or shell and is followed by the numbers in successive rings.

H 1	He 2	Li 2,1	Be 2,2	B 2,3	C 2,4	N 2,5	O 2,6	F 2,7,
Ne 2,8	Na 2,8,1	Mg 2,8,2	Al 2,8,3	Si 2,8,4	P 2,8,5	S 2,8,6	Cl 2,8,7	
A 2,8,8	K 2,8,8,1	Ca 2,8,8,2	Sc 2,8,8,3	Ti 2,8,8,4	V 2,8,8,5	Cr 2,8,8,6	Mn 2,8,8,7	

The number of electrons in the external shell (valency electrons) corresponds to the positive valency of the element and is constant for any particular period. An outer shell of eight electrons, which is found in the inert gases, is supposed to be very stable, and so account for the chemical inactivity of these substances. It must be emphasized that these numbers are only conjectures based upon the chemical properties of the elements. The chemist only concerns himself with the type of atom-model which is in accordance with his knowledge of chemical reactions, and his conclusions are not always in agreement with those based on physical data. One example of this is the periodicity of the Röntgen rays which does not coincide with the chemical periodicity of the elements. Another case is that of sodium, which, in the table above is given the structure 2, 8, 1; Debye on the other hand has brought forward strong physical evidence for the view that the sodium atom contains an inner ring of three electrons.

Since these great divergences of opinion exist, it would serve no useful purpose to give here a detailed account of the various structures which have been assigned to the atoms of the elements. The main outlines of atomic structure have been worked out for us by the physicist, who, however, finds himself faced with a number of unsolved problems as soon as he begins to consider the question in detail. The Rutherford-Bohr atom-model has certainly given us a much clearer conception of the nature of atoms. Many attempts have been made to extend this theory and bring it into harmony with a number of different phenomena by ascribing to the electrons elliptical or very eccentric (comet-like) paths; in spite of all these efforts the study of atomic structure is still far from attaining its ultimate goal of predicting and calculating the chemical and physical properties of the elements from the structure of their atoms. In this connection considerable importance must be attached to the judgment of a physicist (W. Kossel), who has done a great deal of work on the problem of uniting

the physical and chemical conceptions of the structure of atoms and molecules. Kossel declares that the further development of atom-models is a difficult problem, "the solution of which probably depends upon a few fundamental principles. These are as yet not clearly defined and to discover them it will be necessary to utilize every indication derived from many different types of phenomena." Bohr himself has recently stated that to-day "the original assumption that the electrons in the normal state of the atom move in specially simple geometrical orbits, e.g. rings of electrons, can no longer be maintained."

### *The Dualistic Theory*

Every chemist is familiar with the famous "dualistic theory" of chemical affinity which was developed by Berzelius many years ago, and aroused a great deal of controversy. According to this theory chemical combination consists of the mutual saturation of opposite kinds of electricity. Reacting atoms or groups of atoms are supposed to carry an electrical charge, which is the cause of their mutual attraction. In this way one can explain, for example, why sodium reacts vigorously with oxygen, for the latter element is strongly electronegative while sodium is strongly electropositive. The quantities of electricity in the two kinds of atoms need not necessarily be equal, and in sodium there is supposed to be an excess of positive electricity still unneutralized by the negative charge of the oxygen. This gives a reason for the well-known fact that sodium oxide can combine with negative groups, e.g. acid radicles. Berzelius attempted to arrange all the elements in an electrochemical series which would indicate their relative content of electricity. He also tried to apply these conceptions to organic chemistry, but here found himself in difficulties, since, for example, the positive hydrogen atoms in methane could be readily replaced by chlorine, which is strongly negative.

### *Unitary Theory*

In 1839 Dumas replaced the "dualistic theory" of Berzelius by the so-called "unitary" theory. The laws of chemical affinity and valency were first worked out with reference to organic chemistry and even in later times the properties of

carbon compounds have occupied a prominent position whenever the subject has been discussed. This is unfortunate, since we know to-day that carbon differs from all the other elements in the simplicity and symmetry of its valency relationships. These properties endow the carbon atom with the capacity to form an enormous number of compounds, all of which the organic chemist can formulate by the use of simple devices, e.g. valency bonds. These simple methods of formulation are quite inadequate to describe the compounds of other elements.

*Radicle and Type Theories, etc.*

The "radicle" and "type" theories classified compounds with reference to certain fundamental types. Frankland's investigations on organo-metallic compounds were the origin of the ideas of valency and atomicity and led to the discovery of the tetravalency of carbon and the development of structural chemistry. In 1860 Butlerow first used the word "structure" in the modern sense and pointed out how the arrangement of atoms in the molecule might be determined. About the same time Kekulé published the first structural formula. The expression "unsaturated compound" came into use, and in 1865 Kekulé published his formula for benzene which has led to so many new discoveries and theories. A few years later Wislicenus began to speak of the necessity of considering the space arrangement of atoms in the molecule and in 1877 Van't Hoff published "*La chimie dans l'espace*" and defined the laws of the asymmetric carbon atom.

*Theories of Kekule, Baeyer, Thiele, and Werner*

It was soon found that the conception of rigid directed valencies failed to account completely for experimental results. Thus Kekulé's formula for benzene with its alternate single and double linkages predicted the existence of two ortho-di-substitution products while no such isomeric compounds were known. Many hypotheses were devised to remedy these defects, e.g. Kekulé's theory of oscillating valencies which has been revived recently by A. von Weinberg, and the conception of "tautomerism" or "desmotropy" which accounts for certain phenomena by the existence of two isomeric substances which are very readily converted into

one another. Other extensions of the simple valency theory are Baeyer's theory of the "strain" set up when carbon valencies are distorted from their natural tetrahedral arrangement, and Thiele's theory of partial valency, which assumes that an excess of affinity remains, even when all the ordinary valencies of an atom are satisfied. In organic chemistry these divergences from the results expected on the simple theory of valency were only met with in special cases while in inorganic chemistry they were the rule rather than the exception. One is driven to the conclusion that the affinity of an element cannot be divided into units associated with separate valency bonds. This conception of undivided valency was stated by Claus as early as 1881, and ten years later Werner developed a very comprehensive theory on this basis. He does not discuss the arrangement of valencies, but regards the atom as a sphere surrounded by a "binding layer" which replaces the separate valency bonds. The dimensions of this layer are supposed to vary with the type of combination. According to Werner, when all the ordinary valency relationships are satisfied there may still remain an excess of affinity which may cause the formation of "compounds of a higher order." The formation and stability of these compounds is determined by the number of atoms which can arrange themselves in space around a "central" atom.

The difference between the chemistry of carbon and that of other elements is largely due to the fact that this element exhibits the same valency when bound to positive atoms or groups of atoms, e.g. hydrogen, as it does when bound to negative atoms, e.g. oxygen or the halogens. Silicon is the only other element which possesses this property of equal positive and negative valencies; in other cases the atoms have different valencies for positive and negative elements. Thus sulphur has a valency of 2 for hydrogen ( $\text{H}_2\text{S}$ ), but towards oxygen and the halogens it can exhibit a valency of 6 ( $\text{SO}_3$ ,  $\text{SF}_6$ ). In 1900 an exhaustive study of these valency relationships was made by Abegg and Bodländer, who showed that the sum of the "hydrogen" and "oxygen" valencies is always 8.

Highest hydrogen compound	.	$\text{Si}^{\text{IV}}\text{H}_4$	$\text{P}^{\text{III}}\text{H}_3$	$\text{S}^{\text{II}}\text{H}_2$	$\text{Cl}^{\text{I}}\text{H}$
Highest oxygen compound	.	$\text{Si}^{\text{IV}}\text{O}_2$	$\text{P}_2^{\text{V}}\text{O}_5$	$\text{S}^{\text{VI}}\text{O}_3$	$\text{Cl}_2^{\text{VII}}\text{O}_7$

This relationship is not true for boron, whose hydrides had not been discovered at the time when the Abegg-Bodländer rule was first published. These investigators gave the name "normal valency" to the smaller maximum valency of an element, or what is usually regarded as its "strongest" valency; the other valency was termed the "contra-valency."

### *Older Views of the Nature of Valency*

Many different views have been held as to the physical nature of valency forces. Knoevenagel and many other workers thought that valency was due to forces akin to those of gravitation. Certain valency relationships, e.g. those of nitrogen, have been explained by assuming a special shape for the atom (C. A. Bischoff, etc.), or particular positions from which the valency bonds diverge (e.g., Hinsberg's "valency centres"). For the most part, however, chemists have followed Berzelius in ascribing valency to electrostatic forces, and attempt to account for particular reactions in terms of the more or less positive character of the atoms or groups of atoms which take part in the reaction. Vorländer, for example, has recently used a theory of this kind.

### *Recent Theories*

During the last ten years a very comprehensive piece of work on the valency problem has been carried out by Stark. He assumes that a particular atom contains a fixed number of valency electrons set in definite positions, and calculates the chemical binding force from the attraction between the electrons and the positive spheres of its own nucleus and those of neighbouring atoms. His work is therefore an attempt to describe the chemical relationships of atoms in terms of electrical fields of force.

The new atom-models have given us a new and different conception of the manner in which atoms combine together. The tendency exhibited by an atom to form compounds with other atoms is now ascribed to an inclination of certain systems of electrons to revert to a more stable configuration. This is as far as we can go with certainty at the present time; we cannot help thinking, however, that it is along this line of thought that we shall ultimately reach a complete explanation

of atomic and molecular structure. One argument for this view is the degree of success which has already been attained by the attempt to describe the properties of an atom from this standpoint.

### *The Hydrogen Molecule*

The models of the hydrogen atom and molecule worked out by Bohr and Debye on the basis of the Quantum theory probably give us a picture of the hydrogen molecule which is very close to the truth. These models account quantitatively for many of the experimentally determined properties of hydrogen, but in some cases, e.g. the heat of formation of hydrogen molecules, they lead to results which are not in agreement with the values found by experiment. According to these models, the valency bond in the chemical formula of a hydrogen molecule consists of a ring of two electrons, E, E, which move in an orbit at right angles to the line joining the two nuclei H, H, and remain always separated by an angle of  $180^\circ$  C. (see Fig. 16). The distance between the nuclei is about  $10^{-8}$  cms., and the diameter of the electron ring  $0.5 \times 10^{-8}$  cms. It can be shown that such a ring of electrons exerts a binding force which overcomes the mutual repulsion of the nuclei. The process by which a hydrogen molecule is formed is supposed to be as follows. As two atoms approach one another, each electron is attracted away from its own nucleus by that of the approaching atom; this process goes on until the orbits of the two electrons coincide when the formation of the molecule is complete. The stability of such systems can be calculated, and it can be shown, for instance, that the molecule He—He is unstable.

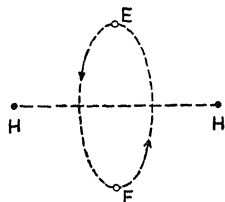


Fig. 16.

### *Kossel's Theory*

A very general theory of molecular binding and chemical valency which covers a wide range of chemical phenomena was developed in 1916 by an eminent physicist, W. Kossel. This theory only deals with one side of the subject, but in spite of this we shall consider it at some length since it has led to important advances which are of particular interest to chemists.



The later theories of Kohlweiler (1918), and of Lacomblé, Langmuir, and Teudt (1919), were based on Kossel's work, and have little advantage over it, at least from the standpoint of chemistry. The most important papers which Kossel has published on this subject are:—"Über Molekülbindung als Frage des Atombaus," ("Atomic Structure and the Formation of Molecules"), *Ann. der Physik*, 1916, (4), 49, 229; and "Über die physikalische Natur der Valenzkräfte" ("On the Physical Nature of Valency Forces"), *Die Naturwissenschaften*, 1919, 7, 339, and 360. Since Kossel's theory is based primarily upon chemical considerations, namely, the periodic system, and the data collected by Abegg and Bodländer and by Werner, it is well adapted for dealing with chemical problems. In its fundamental assumptions it runs parallel with the theories of Berzelius and Werner.

### *Non-polar Bindings*

Kossel, following Abegg, distinguishes between two types of compound, namely "non-polar" compounds, e.g. H—H and N—N, which are formed from atoms of the same sign, and "polar" compounds, e.g. H—Cl, which are made up of differently charged atoms. Non-polar valencies are ascribed to the fusing together of rings of electrons in a similar manner to that described above in the case of the hydrogen molecule.

### *Polar Bindings*

Kossel gives the following explanation of polar valency bonds. When two neutral atoms react their systems of electrons rearrange themselves to form a more stable grouping. This is brought about by an exchange of electrons producing electrically charged ions which are held together in the molecule by electrostatic forces. It has already been stated (see p. 68) that the inert gases probably contain an extremely stable system of electrons, which accounts for their chemical inactivity. As the table of the electronic structure of the elements (repeated here) shows this consists of an outer shell

H 1	He 2	Li 2.1	Be 2.2	B 2.3	C 2.4	N 2.5	O 2.6	F 2.7
Ne 2.8	Na 2.8.1	Mg 2.8.2	Al 2.8.3	Si 2.8.4	P 2.8.5	S 2.8.6	Cl 2.8.7	
A 2.8.8	K 2.8.1	Ca 2.8.8.2	Sc 2.8.8.3	Ti 2.8.8.4	V 2.8.8.5	Cr 2.8.8.6	Mn 2.8.8.7	

of eight electrons in the case of neon and argon. The members of this family with a higher atomic weight probably contain

a larger number of electrons in their outer shell, which, however, exhibits a similar stability. We shall only discuss here the simpler properties of the first series of elements, and shall assume that neon and argon possess an outer shell of eight electrons.

It has been suggested earlier by Van den Broek that a stable shell of eight electrons might be formed from other electronic systems by a rearrangement involving the loss or gain of an electron from one or other of the original atoms. Thus a fluorine atom which (see table) possesses a system with an outer shell of seven will tend to stabilize itself by taking up another electron to form a fluorine ion which would possess the neon system of 2, 8 electrons. This addition of an electron corresponds to one negative valency, or the capacity to combine with a monovalent positive atom. In a similar manner the sodium atom with its system of 2, 8, 1 electrons tends to lose an electron, and pass into system 2, 8 of the sodium ion  $\text{Na}^+$ , so that sodium has one positive valency. Similarly, an atom of oxygen tends to gain two electrons, an atom of magnesium to lose two, an atom of nitrogen to gain three and so on. In general the atoms of the elements in a series tend to lose or acquire electrons so as to form the outer shell which is possessed by the inert gases at the beginning and end of the series. Thus phosphorus may either take up three electrons to form the argon grouping and thus exhibit three negative valencies, or it may lose five electrons, leaving the neon grouping, and will then exert five positive valencies. In the case of carbon and to a less extent with silicon—in which other factors, e.g. the stronger positive character of the nucleus, come into play—there is an equal tendency for the loss or gain of electrons, which is in accord with the known symmetry of the valency relationships of this element.

On these lines we can construct a table of the maximum positive and negative valencies which the elements of the first series should exhibit.

	He	Li	Be	B	C	N	O	F
Positive Valency . . . . .	0	1	2	3	4	5	6	7
Negative Valency . . . . .	0	(7)	(6)	(5)	4	3	2	1

It should be mentioned that a negative valency of more than

four is never realized experimentally. These valency numbers coincide with Abegg's Principle and Contra-valencies for which Drude suggested an explanation along these lines fifteen years ago.

Let us return to fluorine and sodium. When these two elements combine, the loose electron from the outer shell of the sodium atom (2, 8, 1) is given up to the fluorine atom (2, 7) so that the ions  $\text{Na}'$  and  $\text{F}'$  are formed, which both possess the stable outer shell of eight electrons. These ions are held together by electrostatic forces of attraction to form the molecule, and an assemblage of such associated ions constitutes a crystal of sodium fluoride. In this and similar cases, e.g.  $\text{HCl}$  and  $\text{CaO}$  which will be considered later, the chemical binding force is produced by the formation of these stable shells of eight electrons.

More complicated compounds can be accounted for in a similar fashion. For example, the molecule of sulphuric acid,  $\text{H}_2\text{SO}_4$ , contains four divalent negative oxygen ions which altogether have acquired eight electrons, six of these coming from the sulphur atom, which has six positive valencies, and one from each of the two univalent positive hydrogen atoms.

From these considerations one would expect to find the most strongly polar atoms or the most chemically active elements in the immediate neighbourhood of the inert gases; this is true throughout the periodic system.

### *The Strength of the Linkages*

The combination of atoms to form a polar compound is supposed by Kossel to take place in two stages, the electrons being first exchanged, followed by a close approximation of the two ions produced, which are held together by electrostatic forces. A neutral molecule must contain an equal number of positive and negative charges, hence positive and negative valencies appear to saturate one another. The potential of the charge on the ion produced by the loss or gain of an electron is a measure of the attractive force with which the ions are held together, or of the work which would have to be done to separate them.

The firmness of the linkage depends upon magnitude of the

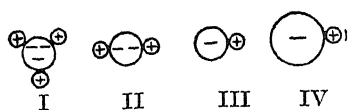
charge and on the volume of the ion. A small ion carrying a given charge can get closer to the centre of gravity of another ion than would be possible for a larger ion carrying the same charge. In this respect the hydrogen ion stands apart from all the other ions which are concerned in chemical reactions; a hydrogen ion has a diameter of only  $10^{-12}$  cms., while that of most other ions is much larger, namely,  $10^{-8}$  cms. Kossel deduces that this causes a hydrogen ion to be held nearly twice as firmly as an ion with the same charge, but of the usual size.<sup>1</sup>

These preliminary considerations enable us to discuss now the part of Kossel's work which most concerns chemists. This is the discussion of the arrangement and magnitude of the electrostatic binding forces which are concerned in the formation and decomposition of certain molecules. Kossel assumes that, owing to the rapid motion of the external electrons around the nucleus, the electrical forces which produce the attraction between ions are symmetrically distributed and in all his calculations regards the "centre of gravity" of these forces as situated at the centre of a spherical ion. He thus uses the conception originally due to Werner of describing chemical affinity as the effect of forces from a centre and not separate forces for each valency bond. He does not take into account the electrodynamic (magnetic) forces which are due to the motion of the electrons, and which must have some influence on the stability of the molecule.

According to Kossel the firmness of the union between the parts of a molecule and therefore the amount of work which would have to be done to separate its ions (the Dissociation Potential) is determined by the charges and volumes of the ions concerned. In the diagrams used here, the small circle inscribed with a + sign indicates the small hydrogen ion, the larger circles enclosing one or more - signs represent the larger negative ions of other elements. The ratio of the diameter of one of these ions to that of a hydrogen ion is very much larger (10,000 : 1) than is indicated by the relative sizes of the circles in the diagram. From these definitions it will be seen that I represents an ion with three negative charges

<sup>1</sup> The  $\alpha$  particle or helium ion  $\text{He}^{++}$  is of about the same size, but does not appear to take part in any chemical reactions.

combined with three hydrogen ions. These are more firmly held than the hydrogen ions in II, which are combined with an ion of the same size carrying only two charges. In III

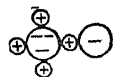


the hydrogen is less firmly bound than in II, for while the ion is still of the same size the charge has diminished to one

unit, and a still weaker linkage is represented by IV, in which one charge is carried by an ion of greater diameter.

Under certain conditions a neutral molecule may arrange itself alongside another neutral molecule. Kossel's theory of the formation of complex molecules in general shows a strong resemblance to Werner's theory, but leads to definite quantitative conclusions about these substances. A simple example of complex formation is given by the formation of ammonium chloride  $\text{NH}_4\text{Cl}$  from ammonia  $\text{HN}_3$  and hydrochloric acid  $\text{HCl}$ . The annexed diagram shows the arrangement of the  $\text{NH}_4\text{Cl}$  molecule: all four hydrogen ions

are bound in a similar manner to the central nitrogen atom. While one of the hydrogen ions in the diagram appears to be specially situated between the nitrogen and chlorine nuclei, this is simply due to the limitations of the graphical method of representation which is not capable of indicating the motions of the constituent particles of the molecule. All four hydrogen ions, including the one derived originally from the hydrochloric acid, are held with the same firmness by the attraction of the trebly charged nitrogen ion  $\text{N}'''$  and the singly charged chlorine  $\text{Cl}'$ . The dissociation of the molecule which takes place when ammonium chloride is dissolved in a solvent with a high dielectric constant, e.g. water, is described completely by the equation  $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4' + \text{Cl}'$ ; that is, the ion  $\text{Cl}'$  which in the molecule is repelled by the trivalent ion  $\text{N}'''$  separates from the residue  $\text{NH}_4'$ .



### *The Hydrides of the Non-metals*

These considerations lead to a generalization which is verified by experiment, and which may be put in the following form. The greatest tendency to form complex molecules is exhibited by those ions which exert the greatest attractive

force on surrounding ions, or in other words, by the ions with a large electric charge, and a small volume. From this point of view one can readily account for many of the peculiar properties of aqueous solutions by the position which is taken by water in the series of hydrides of the non-metals. A number of these hydrides are shown in the table on this page.<sup>1</sup> The negative charge on the central ion decreases from left to right (from N to F), as is shown by the small diagrams at the foot of each column, and the atomic volumes increase as one passes down a vertical column (from N to Sb).

←			
↑	NH <sub>3</sub>	OH <sub>2</sub>	FH
	PH <sub>3</sub>	SH <sub>2</sub>	CH
	AsH <sub>3</sub>	SeH <sub>2</sub>	BrH
	SbH <sub>3</sub>	TeH <sub>2</sub>	IH

The firmness with which the hydrogen ions are held increases in the directions shown by the arrows, and is greatest in ammonia, and least in hydriodic acid. This is exactly in accordance with the order in which these hydrides can lose a hydrogen ion and exhibit acidic properties. Water can abstract a hydrogen ion from all the hydrides which are found to the right of it or below it in the table. The reaction is precisely similar to that involved in the formation of ammonium chloride, and in the case of H<sub>2</sub>O and HF (see diagram I) leads to the formation of the ions F' and H<sub>2</sub>OH', or the fluorine ion and a hydrated hydrogen ion. Ammonia reacts with water as shown in dia-

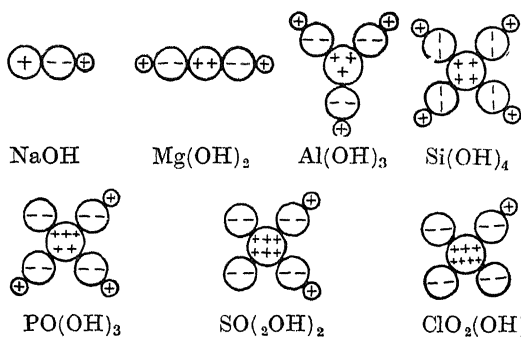


gram II, giving the ions NH<sub>4</sub>' and OH' ; PH<sub>3</sub> does not take part in a similar reaction because the volume of the P''' ion is greater than that of N''', and consequently this ion does not

<sup>1</sup> The limitations of this graphical method of representation must again be emphasized. The drawings should not be taken to indicate the actual arrangement of the atoms in the molecule in every detail. It has already been stated that the parts of the molecule are in rapid motion not indicated in the formulae, which are incomplete in other respects. Thus certain physical properties of water (specific heat, moment of inertia) seem to show that the hydrogen ions are arranged unsymmetrically about the oxygen ion.

exert so large a force of attraction on the hydrogen ion of the water.

An instructive but more complicated example is given by the series of hydroxides sodium hydroxide,  $\text{NaOH}$ , magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , orthosilicic acid,  $\text{Si}(\text{OH})_4$ , orthophosphoric acid,  $\text{PO}(\text{OH})_3$ , sulphuric acid,  $\text{SO}_2(\text{OH})_2$ , and perchloric acid,  $\text{ClO}_3(\text{OH})$ . The diagrams alongside show the arrangement of the ions in these molecules.



Two types of dissociation are possible: (1) a division between the central ion and an oxygen ion, i.e. the splitting off of a hydroxyl ion, (2) the separation of a hydrogen ion from an oxygen ion. The

first is a basic reaction, the second gives acid properties to a substance. The number of positive charges on the central ion increases continually as one passes from sodium to chlorine, and this causes the oxygen ions to be held more and more firmly while the force holding the hydrogen nuclei diminishes. This is exactly the order of increasing acidity of these hydroxides. Kossel has used this series to make a quantitative test of his theory, and from the laws of electrostatics has calculated the energy required to split off a hydrogen ion or a hydroxyl ion from each of these substances. To simplify matters he assumes that all the ions concerned have the same radius except the hydrogen ion, which he takes as negligibly small. As unit of dissociation potential he takes the work necessary to separate two univalent ions which have the same radius as that assumed for  $\text{Na}^+$ ,  $\text{Mg}^{++}$ , etc. The results of these calculations are shown graphically in Fig. 17. The dotted line represents the work required to dissociate water into hydrogen and hydroxyl ions. The curves can scarcely be expected to agree exactly with experimental data since the assumptions made to simplify the problem are

probably not strictly true. Generally speaking, however, these curves are in good agreement with the chemical properties of the substances concerned. Thus for sodium hydroxide the dissociation potential for the liberation of a hydroxyl ion is only half the corresponding potential for the liberation of a hydrogen ion:  $\text{NaOH}$  should, therefore, dissolve in water to form an alkaline solution. The curves showing the dissociation potentials for hydrogen and hydroxyl ions cross in the middle of the series, so that in this region the work required to split off either kind of ion is approximately the same. This should correspond to compounds which can react either as an acid or as a base, or what are termed "amphoteric" electrolytes. Aluminium hydroxide is a well-known member of this class of substances.

It has already been stated that the simple methods of calculation employed here cannot be expected to lead to results in exact agreement with those obtained by experiment. Nevertheless, this attempt by Kossel to account for chemical forces in terms in electrostatics must be regarded as a most promising step forward. Throughout his work he adopts the old conception of Berzelius that chemical affinity must ultimately be described in terms of electrical forces.

Kossel also adopts Werner's view that it is spatial considerations which play a prominent part in determining the number of ions which can be arranged in a stable system about any particular ion.

Fig. 18 shows some examples of molecular structure which, according to Kossel, are brought about by the fusion of outer shells of electrons and the subsequent rearrangement of electrical charges. The outer ring or shell of eight electrons in the argon atom is found again in the molecules of hydrochloric acid and calcium oxide. The figure shows only the valency electrons which form this eight-membered ring, and exert a binding force upon the residues of the atoms. In the

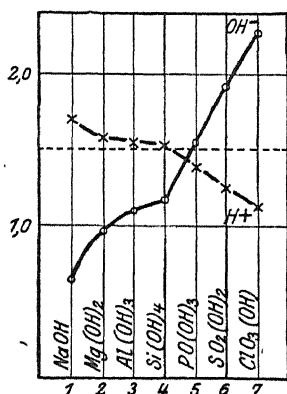


Fig. 17.



hydrochloric acid molecule Kossel calculates from the relative charges on the residues that the ring is in equilibrium very close to the chlorine nucleus when it occupies a plane which is at right angles to the line joining the two nuclei, and which divides this line in the ratio of more than 100 : 1.

Fig. 18 also shows Kossel's model of the nitrogen molecule, which is an example of a "non-polar" binding. He assumes that the stable ring of electrons contains, in the molecule of nitrogen 10, in that of oxygen 12, and in that of chlorine 14 electrons, which are symmetrically arranged between the two

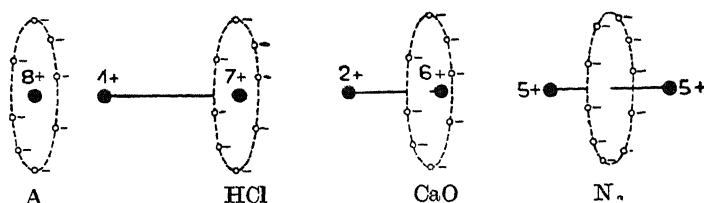


Fig. 18.

similar nuclei. For these systems of electrons the analogy of the inert gases, with their eight-membered ring or shell can no longer be employed. These models carry us much further into the region of speculation ; we are therefore not surprised to find that other physicists have come to different conclusions about the structure of these molecules. For instance, Sommerfeld has deduced from the optical properties of nitrogen that the molecule of this gas contains two nitrogen nuclei, which each carry seven positive charges. Each nucleus is surrounded by four firmly held electrons, while six more loosely-bound electrons form a ring between the two nuclei and hold them together. It will be noted that while this model differs in many respects from that of Kossel it still retains the idea of a binding ring of electrons. Against this view must be quoted the work of Debye and Scherrer, who state that their Röntgen ray photographs of diamond give no indication of the existence of a ring of electrons between the carbon atoms. These discrepancies can only be explained by much further experimental work. Fortunately physics now offers to us many different methods of attacking the problem. The detailed study of crystals by the most modern methods enables us to

investigate the properties of ions without the hindrance of such complications as the effect of a solvent, etc. Other promising lines of investigation are the study of compressibility of the characteristic frequencies of atoms, of Röntgen rays, and many other properties.

### *Conclusion*

The study of atomic and molecular structure is therefore at present in a state of rapid development. Radiochemistry has provided us with a rough model of the structure of atoms which, while still incomplete, has already thrown a great deal of light on many of the problems of the fine structure of matter. The amazing progress which has been made in this branch of science is a striking tribute to the usefulness of modern methods of research. This is no less true of the younger branch of Röntgen ray optics. In both cases the work of many investigators in different countries, each assisting the other in the pursuit of knowledge, has brought about, in a very short space of time, a complete elucidation of many difficult problems and a correlation of the newer work with the older branches of science.

In our knowledge of the laws of the structure of atoms and molecules we have not yet attained the same degree of success. It is, indeed, astonishing to see how far human ingenuity has enabled us to penetrate into the mysteries of the microcosm which, even ten years ago, seemed to be an impregnable citadel. The ultimate aim of this branch of science is the interpretation of all the properties of the elements in terms of the structure of their atoms, just as the organic chemist accounts for the properties of many complicated organic substances in terms of the structure of their molecules. There will probably be a number of conflicting theoretical interpretations of the experimental material from which there will finally emerge one triumphant atom-model. This model, if based on the principles of modern physics will, inevitably, be very complicated. It may later be displaced by a new Copernicus who will substitute a few simple fundamental principles which govern these complicated planetary systems in the atom. This does not, however, appear very probable. Recent history shows that science has made most of its advances by the collaboration

of a large number of workers and critics, and by the elaboration of special methods of investigation; consequently it is only very rarely that any of the forward steps have had to be retraced.

The lion's share in the further development of this subject will probably be appropriated by physics. In many cases further advances can only be made by utilizing the most delicate and powerful physical methods of attack. This is particularly true for the further investigation of optical and Röntgen ray phenomena, the elucidation of the "quantum" relationships of spectra, the discovery of the missing rays between the Röntgen and ultraviolet rays, the liberation of loosely-bound electrons by light, of different wave-lengths, the further study of the effect of electrical and magnetic fields upon electrons, the correlation of thermodynamic observations, etc. The problems are many. Will they all find solutions in the future? Will the number of patient and unselfish workers still remain as large as it has been up to the present? Will the importance and significance of their work always be appreciated when even now a selfish generation resents the advances which have been made? Or are the present discoveries but harbingers of a wonderful spring-time of science which shall lead to a still greater harvest of knowledge.

The chemist who is not at the same time a physicist, will have to stand aside and view the working out of these things with somewhat mixed feelings. The recent literature of the subject shows all too many examples of the facility with which atomic and molecular structures can be worked out on paper, a task which, until much more experimental work has been done, is entirely unprofitable. This attitude of mind is a retrogression from the standpoint of Baeyer to that of Aristotle, and involves the same wastage of effort as was seen in the numerous attempts to solve the riddle of the periodic system by speculation rather than by experiment. The problems of structural chemistry will not be settled by work of this kind. As A. von Weinberg has said: "The further development of the structural problems of organic chemistry can scarcely be attempted until the problem of the fine structure of electrons in atoms has been solved." It will evidently be some time before practical chemistry reaps many advantages from

the study of atom structure. As yet chemists have obviously little inducement to give up their admittedly formal methods of expressing the ideas of affinity and valency; they will still use the same valency bonds and bracketed formulae as they did before.

Yet chemistry should really go hand in hand with physics in the working out of these problems, for it can considerably enlarge the scope of the argument by bringing in a large range of experimental data. Quite apart from the study of carbon compounds, there is still a large amount of work to be done. Thus the affinity and valency relationships of the other non-metals would prove a profitable field of investigation; the recent work on the chemistry of boron and silicon has shown that many important facts still await discovery in this rather neglected field.

Patient experimental work is worth far more than novel and striking theories. An experimental result, however small, has a lasting value. In the words of Leonardo da Vinci: "Experiments cannot err, they may correct our errors." The usefulness of theories should not be exaggerated; they may pleasantly titillate the mind, but are often merely old wine in new bottles. The real value of a theory is measured by the practical conclusions which may be drawn from it, by the new discoveries and quantitative relationships to which it gives rise. H. Kopp, who once wrote a clear and critical outline of the progress of chemistry, has said, "From the story of chemistry we learn to recognize what are the real servants of science; throughout the whole of its development we see that each piece of work, each new idea which may be quite satisfactory at the time of its inception, is usually only the forerunner of a wider conception which comes with a later increase of knowledge. The best service is rendered by those theories which bear within themselves the germs of such new and wider conceptions." This is still more true to-day. In consequence, I have thought it useful to give some place in this volume to the historical aspect of the subject.

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